THE PROPERTIES OF ELECTRICALLY CONDUCTING SYSTEMS

Including Electrolytes and Metals

BY

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GENERAL INTRODUCTION

American Chemical Society Series of Scientific and Technologic Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on chemical subjects. At the same time it was agreed that the National Research Council, in cooperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical development. The American Chemical Society named as Trustees, to make the necessary arrangements for the publication of the monographs, Charles L. Parsons, Secretary of the American Chemical Society, Washington, D. C.; John E. Teeple, Treasurer of the American Chemical Society, New York City; and Professor Gellert Alleman of Swarthmore College. The Trustees have arranged for the publication of the American Chemical Society series of (a) Scientific and (b) Technologic Monographs by the Chemical Catalog Company of New York City.

The Council, acting through the Committee on National Policy of the American Chemical Society, appointed the editors, named at the close of this introduction, to have charge of securing authors, and of considering critically the manuscripts prepared. The editors of each series will endeavor to select topics which are of current interest and authors who are recognized as authorities in their respective fields. The list of monographs thus far secured appears in the publisher's own announcement elsewhere in this volume.

The development of knowledge in all branches of science, and especially in chemistry, has been so rapid during the last fifty years and the fields covered by this development have been so varied that it is difficult for any individual to keep in touch with the progress in branches of science outside his own specialty. In spite of the facilities for the

examination of the literature given by Chemical Abstracts and such compendia as Beilstein's Handbuch der Organischen Chemie, Richter's Lexikon, Ostwald's Lehrbuch der Allgemeinen Chemie, Abegg's and Gmelin-Kraut's Handbuch der Anorganischen Chemie and the English and French Dictionaries of Chemistry, it often takes a great deal of time to coordinate the knowledge available upon a single topic. Consequently when men who have spent years in the study of important subjects are willing to coordinate their knowledge and present it in concise, readable form, they perform a service of the highest value to their fellow chemists.

It was with a clear recognition of the usefulness of reviews of this character that a Committee of the American Chemical Society recommended the publication of the two series of monographs under the auspices of the Society.

Two rather distinct purposes are to be served by these monographs. The first purpose, whose fulfilment will probably render to chemists in general the most important service, is to present the knowledge available upon the chosen topic in a readable form, intelligible to those whose activities may be along a wholly different line. Many chemists fail to realize how closely their investigations may be connected with other work which on the surface appears far afield from their own. These monographs will enable such men to form closer contact with the work of chemists in other lines of research. The second purpose is to promote research in the branch of science covered by the monograph, by furnishing a well digested survey of the progress already made in that field and by pointing out directions in which investigation needs to be extended. To facilitate the attainment of this purpose, it is intended to include extended references to the literature, which will enable anyone interested to follow up the subject in more detail. If the literature is so voluminous that a complete bibliography is impracticable, a critical selection will be made of those papers which are most important.

The publication of these books marks a distinct departure in the policy of the American Chemical Society inasmuch as it is a serious attempt to found an American chemical literature without primary regard to commercial considerations. The success of the venture will depend in large part upon the measure of cooperation which can be secured in the preparation of books dealing adequately with topics of general interest; it is earnestly hoped, therefore, that every member of the various organizations in the chemical and allied industries will recognize the importance of the enterprise and take sufficient interest to justify it.

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PREFACE

The history of the development of chemistry and molecular physics during the past few decades is largely an account of the growth of our conceptions of matter in the ionic condition. Whatever the shortcomings of the older ionic theory may have been, it has proved itself a powerful tool for the purpose of disclosing the structure of material substances. The intimate relation existing between matter and electricity, first inferred by Helmholtz as a consequence of Faraday's laws, has been established as securely as the atomic theory itself. Present day conceptions as to the nature of matter are, in a large measure, the outgrowth of fundamental conceptions underlying the ionic theory. It is true that certain branches of molecular physics, to the development of which the ionic theory has contributed, have outstripped this theory in the importance of the results obtained. Nevertheless, the further advance of chemistry is largely dependent upon the further development of our conceptions of matter in the ionic condition.

A vast amount of experimental material relating to this subject has accumulated during the past thirty years. It is found scattered through the volumes of many journals and the transactions of scientific societies. Unfortunately, this material has nowhere been collected in a form rendering it available to those who are not primarily interested in this field. The purpose of the present volume is to present the more important of this material in a comprehensive and systematic manner, thus enabling the reader to gain a knowledge of the contemporary state of this subject without an undue expenditure of time and effort. It is hoped, too, that this volume will prove useful to those investigators in allied sciences, who find it difficult to ascertain the precise limitations underlying methods and ideas which they often find it necessary to apply in their own subjects.

The systems treated are those in which ionic phenomena are most clearly in evidence. Metallic systems are included, for, although the nature of the metals is but little understood, the existence of a relation between the phenomena in metallic and electrolytic systems is unmistakable. The treatment of metals is necessarily brief, since our knowledge of them is still very uncertain. The chemical aspects of metallic systems are, so far as possible, kept in the foreground. A more detailed

treatment of the experimental material relating to metals is unnecessary, since much of this has already been collected in various handbooks.

Naturally, the major portion of this volume is devoted to a consideration of the properties of electrolytic solutions. The attempt has been made to present the subject broadly in order to bring out those elements of the phenomena which are common to solutions in all solvents. Solutions in non-aqueous solvents are treated somewhat more extensively than aqueous solutions, since the data relating to these solutions have not been collected heretofore.

The subject is presented from an empirical standpoint, since an adequate theory of electrolytic solutions does not exist. Such theories as have been advanced in recent years give evidence of having been adapted to fit particular cases. In the end, the theory of electrolytic solutions will probably be a composite of various theories which now appear more or less applicable. Such a theory will doubtless embody some of the more fundamental elements of the older ionic theory.

A complete bibliography has not been attempted. References given as footnotes will serve as a key to the literature.

In conclusion, I wish to express my indebtedness to my colleague, Professor B. S. Merigold, for reading the manuscript and to Mr. Gordon W. Browne for his assistance in preparing the figures.

C. A. K.

Clark University,
January 5, 1922.

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THE PROPERTIES OF ELECTRICALLY CONDUCTING SYSTEMS

Chapter I.

Introduction.

1. *Classification of Conductors.* The property of electrical conductance appears to be one common to all forms of matter. The value of the conductance of different forms of matter, however, varies within very wide limits. Thus, the specific conductance of silver has a value of 6.0×10^5, while that of paraffin is 3.5×10^{-19}. The specific conductance of gases under ordinary conditions is scarcely measurable. Naturally, the conductance of any given system depends upon its state; and, in general, any change in the condition of the system will materially affect the value of its conductance.

Conductors may be conveniently grouped into a number of classes, the members of which possess many properties in common.

2. *Gases.* Under ordinary conditions the conducting power of gases is of a very low order, and such conductance as they possess is not an intrinsic property of the gases themselves, but is due, rather, to the influence of external agencies. Thus, under the action of various radiations, gases are ionized and when in this condition conduct the current. This power of conduction, however, is lost when the external source of excitation is cut off. Whether or not the gases themselves may possess in some slight degree the power of conducting the current is uncertain, since the conducting power of gases which have been entirely freed from disturbing effects is of such a low order that the usual methods of measurements fail. The conductance of a gas is a function of its density. It is probable that at high densities gases will exhibit properties comparable with those of many liquids. In the case of hexane it has been shown that the residual conductance on purification is for the most part due to the action of external radiations, which indicates that the conductance, which many liquid substances of low conducting power possess, is not a property of the pure substances themselves.

In gases, as well as in insulating liquids, under the action of external

radiations, we have systems which are not in a state of equilibrium. These systems will not be further considered here, since they have been treated extensively in treatises dealing with the conduction of gaseous systems. In what follows we shall treat only such systems as are normally in a conducting state. These may be divided into two classes; namely, metallic and electrolytic conductors.

3. *Metallic Conductors.* Metallic conductors are characterized by the absence of material effects when a current passes through a system comprising one or more conductors of this class alone. In this respect metallic conductors are for the most part sharply differentiated from electrolytic conductors, in which concentration changes or other material effects accompany the passage of the current through any surface of discontinuity. It does not follow, however, that metallic and electrolytic conduction are entirely unrelated and that the two processes of conduction may not take place more or less simultaneously. Certain substances apparently conduct electrolytically when in one condition and metallically when in another. In other cases, a portion of the current appears to be carried by a process similar to that in the metals and another portion by a process similar to that in electrolytes.

Metallic conductors are also characterized by the relatively high value of their conducting power. While a few metals exhibit a value of the conductance comparable with that of electrolytes, the conductance of most metals is many times greater than that of electrolytes. If this is true at ordinary temperatures, it is even more true at lower temperatures where the resistance may ultimately fall off to practically zero. The problem of metallic conduction is one possessing great interest and one whose solution cannot but prove to be of great importance in the development of chemistry and molecular physics. At the present time, however, its solution appears far from complete. While metallic conductors come within the scope of the present monograph, it is not intended to treat this subject exhaustively.

4. *Electrolytic Conductors.* Electrolytic conductors are characterized, in the first place, by the fact that the passage of the current through them is accompanied by a transfer of matter. In a homogeneous electrolytic conductor this transfer of matter within the body of the conductor does not become apparent, but at any point of discontinuity material effects make their appearance. The material effects accompanying the current are subject to certain definite laws commonly known as Faraday's Laws. Conductors for which Faraday's Laws hold true within the limits of the experimental error are termed electrolytic conductors. We have here to consider two classes of electrolytic conductors:

First, those which conduct the current when in a pure state and, second, those which conduct the current as a result of the presence of other substances. This latter class of conductors is embraced within the term electrolytic solutions.

a. *Electrolytes Which Conduct in the Pure State.* Within this class is included, in the first place, the fused salts. With a few exceptions, the fused salts are excellent conductors of the electric current. Their specific conductance near the melting point being of the order of 1.0, their conductance, therefore, is about 1×10^{-5} that of silver. The salts are compounds between a strongly electronegative and a strongly electropositive constituent, and it is seldom that such substances do not possess the power of conducting the current in a marked degree. As the electropositive or electronegative nature of one or the other of the constituents becomes less pronounced, however, the conductance of the resulting compound is diminished. This is the case, for example, with mercuric chloride.

When hydrogen is combined with a strongly electronegative element or group of elements, the resulting compound, as a rule, exhibits electrolytic properties. This, for example, is the case with water, which has been shown to conduct the current slightly when in a pure state. At 18° its specific conductance has a value of 0.042×10^{-6}. Other compounds of hydrogen exhibit similar properties.

When hydrogen is combined with elements which are less strongly electronegative, the resulting compounds exhibit a lower conducting power. In the case of the hydrocarbons the conductance reaches extremely low values and it is possible that these substances in the pure state do not possess the power of conducting the current.

While substances in the fused state are, as a rule, better conductors than in the solid state, electrolytic conductors are not restricted to the fused state, since certain substances in the solid state have been found to conduct the current quite as readily as the fused salts.

b. *Electrolytic Solutions.* The most common electrical conductors are those in which the conductance is due to a mixture of two or more substances. As a rule, one of these, the solvent, is present in considerable excess and may itself be only a very poor conductor. In this case, the conductance is said to be due to the addition of the second component, termed the electrolyte. To this class belong all the ordinary solutions of salts in water. In some cases an electrolytic solution results when a substance, which itself in the pure state is a poor conductor, is added to a second substance which likewise is a poor conductor in the pure state. As an example, we may cite solutions of the acids in water.

Hydrochloric acid, for example, in the pure state has a conductance even lower than that of water. When dissolved in water, however, the conductance of hydrochloric acid is much greater than that of ordinary salts dissolved in the same solvent. This class also includes solutions of various organic oxygen and nitrogen compounds in the liquid halogen acids. This behavior, moreover, is not restricted to acids, since solutions of many bases, such as ammonia, result from a mixture of two components neither of which possesses considerable conductance in the pure state. Where an electrolytic solution results from a mixture of two components which are themselves non-conductors, it is probable that reaction takes place when the two components are brought together, as a result of which an electrolyte is formed.

Apparently, electrolytic solutions result in all cases when typical salts are dissolved in liquids up to sufficiently high concentrations. The property of forming electrolytic solutions with dissolved salts is thus not peculiar to water or solvents of the water type, but is a property common to all fluid media. It is true that the phenomena are materially altered as the nature of the solvent medium changes, but otherwise, if the solutions are sufficiently concentrated, the order of the conductance values will not differ greatly in different solvents.

Among the various properties of the solvent medium which appear to have a marked influence upon the properties of the resulting electrolytic solution, the dielectric constant stands out as the most important factor. As the dielectric constant of the solvent medium decreases, the conductance of the resulting solutions is altered, but the power to conduct the current is never lost, no matter how low the dielectric constant of the solvent medium may be. Thus, solutions of salts of organic bases in chloroform conduct fairly well.

From the standpoint of the development of chemistry, solutions of electrolytes are of first-rate importance. Electrolytic solutions exhibit a variety of phenomena and admit of a variety of reactions which are not to be found in the case of any other system of substances. A great variety of reactions take place at the electrodes when solutions of electrolytes are electrolyzed, and, when solutions of electrolytes are mixed, reactions take place between the constituent electrolytes. Reactions between electrolytes are characterized by the extreme facility with which they occur. It is only in exceptional cases that the rate of such reactions is sufficiently low to admit of measurement. In solutions of electrolytes, therefore, we are dealing essentially with systems in equilibrium. This is of importance in their theoretical treatment, since thermodynamic principles may be readily applied to systems in equilibrium.

5. *Electricity and Matter.* While electrolytic solutions are thus of great importance from a practical point of view, they have played no less important a rôle in the development of our conceptions of the nature of matter and the nature of chemical reactions. That electricity and matter are intimately related was long since pointed out by Helmholtz as a consequence of Faraday's Law. Since in electrolytes electricity and matter are associated in definite and fixed proportions, and since matter appears to be discrete in its structure, it follows that electricity also must be discrete in its fundamental structure. Corresponding to the atoms, the smallest subdivisions of elementary substances, we have the fundamental charge of electricity, the charge associated with a single univalent ion, which represents the smallest known subdivision of the electric charge. The development of the mechanics of the atoms in the last two decades has greatly enlarged our knowledge of the fundamental relation between electricity and matter. The fundamental charge of electricity, the charge associated with the negative electron, is objectively as real as the atoms and the molecules themselves. The intimate relation of the fundamental charge with the atoms or groups of atoms, which play so important a part in many chemical reactions, makes it appear probable that in chemical reactions the negative electron is primarily concerned. The horizon of chemistry is rapidly broadening in this direction, and a study of electrolytic systems will unquestionably play a great part in the ultimate elucidation of the mechanics of chemical reactions.

6. *The Ionic Theory.* To account for the various phenomena which have been observed in electrolytic solutions, the ionic theory has been introduced. While ordinarily the ionic theory is supposed to include fundamentally those concepts first introduced by Arrhenius, this theory is, in fact, a composite theory in which many molecular mechanical hypotheses are combined. It is to Arrhenius that is due the credit of first having developed a theory of electrolytes, quantitative in its nature, the correctness of which it was possible to determine by exact quantitative methods. While the gaps left in the theory of electrolytic solutions by the work of Arrhenius may not be overlooked, it should not be forgotten that up to the present time no other theory has been proposed which is equally well able to account for so many and for so large a variety of facts.

The introduction of the theory of Arrhenius has, from the start, met with the most determined opposition on the part of many chemists. It is interesting, now, to note that in recent years the basis of the objections to the theory of Arrhenius has greatly shifted and many of the originally proposed objections have since been found to be without foundation.

Nevertheless, the opposition to the theory of Arrhenius has continued to find supporters even up to the present time. In part, at least, this opposition has been due to a realization on the part of chemists of the limitations of the theory of which its author has himself been aware. One of the fundamental truths which the theory of Arrhenius has brought to the attention of chemists is the existence of equilibria in electrolytic systems; and, however the details of his theory may subsequently be modified, it would appear that this most fundamental element of his theory must always be retained.

Chapter II.

Elementary Theory of the Conduction Process in Electrolytes.

1. *Material Effects Accompanying the Conduction Process.* That material effects accompany the passage of the current through a non-metallic medium was known at an early date. Thus Nicholson and Carlisle [1] observed the decomposition of water, and Sir Humphrey Davy [2] isolated the element potassium by electrolysis of the hydroxide. While it was thus recognized that chemical action is intimately associated with the passage of the current through an electrolyte, the quantitative relationships were not studied until Faraday carried out his classical researches. It is unnecessary to give here in detail the results of Faraday's investigations. It will be sufficient to state the laws which now bear his name; namely, that chemical action accompanying the passage of the current is proportional to the quantity of electricity passing, and that, for a given quantity of electricity, the chemical effects in the case of different reactions are equivalent. These laws have since been verified by a multitude of observations on the action of the current passing through electrolytes. The most exact measurements have been made on the deposition of silver and on the liberation of iodine.[3] In all cases, Faraday's Law has been found to hold within the limits of experimental error. It has been found to hold in the case of fused salts at higher temperatures,[4] as well as in that of certain solid electrolytes.[5]

There are cases, indeed, where apparent exceptions to Faraday's Law appear. For example, when a current is passed through a solution containing a compound of sodium and lead in equilibrium with metallic lead, there are deposited on the anode 2.25 equivalents of lead per equivalent of electricity.[6] Similar results have been obtained in the case of solutions of certain other metallic complexes in liquid ammonia.[7] These cases, however, do not constitute an exception to Faraday's Law, since there are present in these solutions, presumably, a series of complexes

[1] Nicholson and Carlisle, *Nicholson's Jour.* *4*, 179 (1800); *Gilbert's Ann.* *6*, 340 (1800).
[2] *Phil. Trans.* *100*, 1 (1808).
[3] Bates and Vinal, *J. Am. Chem. Soc.* *36*, 936 (1914).
[4] Richards and Stull, *Proc. Am. Acad.* *38*, 409 (1902).
[5] Tubandt and Lorenz, *Ztschr. f. phys. Chem.* *87*, 513 (1914).
[6] Smyth, *J. Am. Chem. Soc.* *39*, 1299 (1917).
[7] Peck, *J. Am. Chem. Soc.* *40*, 335 (1918).

whose average composition corresponds to the reaction which occurs at the electrode on electrolysis of these solutions. The precipitation at the anode in these solutions corresponds to the average composition of the complex.

The solutions of the alkali metals and the metals of the alkaline earths in liquid ammonia constitute another apparent exception to Faraday's Law, and in order to reconcile the results obtained in the case of these solutions with Faraday's Law it is necessary to extend it.[8] When, for example, a current is passed through a solution of sodium in liquid ammonia, only a fraction of the current appears to be accompanied by an observable material process. These solutions, therefore, behave as though the current were in part carried by an electrolytic and in part by a metallic process. In order to reconcile these results with Faraday's Law, it is necessary to assume that the process of metallic conduction is likewise an ionic one, the current in this case being carried by the negative electrons. If this hypothesis is made, then Faraday's Laws hold in these cases also.

Faraday's Laws lead to important conclusions, not only with regard to the mechanism of the conduction process in electrolytes, but also with regard to the relation between electricity and matter. Interpreted from a molecular kinetic point of view, Faraday's Laws state that definite fixed quantities of electricity are associated with definite amounts of matter. As Helmholtz[9] pointed out, if matter consists of discrete particles, then electricity likewise is discrete in character. Corresponding to the atom, the smallest subdivision of matter, we have a fundamental electric charge, namely, the charge on a univalent ion. The charge, therefore, on any given particle of matter, whether it be of molecular or atomic dimensions or whether it be of larger dimensions as, for example, a drop of oil, may not be varied continuously but only in multiples of the unit charge. The discontinuous nature of the electric charge is one of the fundamental facts underlying electrochemical phenomena and must be taken into account in the interpretation of these phenomena.

The reactions accompanying the passage of the current through an electrode surface indicate clearly that an intimate relation exists between chemical and electrical phenomena. Berzelius[10] attempted to account for the structure of chemical compounds by means of an electrical hypothesis. In this, however, he was unsuccessful, largely because he assumed a false mechanism as representing the association between electricity and matter. Instead of associating the charge with the atoms

[8] Kraus, *J. Am. Chem. Soc.* *30*, 1323 (1908); *36*, 864 (1914).
[9] Helmholtz, *J. Chem. Soc.* *39*, 277 (1881); *Wiss. Abh.* *3*, p. 52.
[10] Berzelius, *Lehrbuch*, Ed. 3, Vol. 5 (1835); Ostwald, *Electrochemie*, p. 335.

themselves, in his theory, he associated the charge with certain atomic complexes, which complexes in fact do not exist. Present day conceptions regarding the constitution of chemical compounds do not differ in many respects from those of Berzelius save that it is assumed that the charge is associated with the atoms. In recent years, as a result of experimental methods which have enabled us to gain an insight into the structure even of the atoms themselves, it is becoming more and more apparent that, in their compounds, the elements exist not in an atomic, but in an ionic, that is, in a charged, state. Under ordinary conditions this state of the elements in a compound is not clearly evidenced, except in the case of such compounds as are electrolytes when dissolved in suitable solvents or when in a fused state. From the standpoint of chemistry, the study of the properties of electrolytes is therefore not so much an end as a means. In other words, the study of the properties of electrolytes constitutes a convenient method of acquiring knowledge regarding the constitution of various chemical compounds.

Faraday was not content to merely state the results of his observations and to combine these observations in the form of general laws. He attempted to gain an insight into the mechanism of the processes involved. It is often assumed that the ionic theory dates from the time when Arrhenius co-ordinated the work of earlier investigators and suggested a means for determining the relative amount of carriers present in an electrolytic solution under given conditions. The ionic theory, however, is much older than this. Its foundation was laid by Faraday,[11] who recognized that in an electrolyte the current is carried by positive and negative electrical charges associated with definite material complexes moving in opposite directions through the solution. The terms which we now employ to describe the phenomena observed in the passage of the current through an electrolyte are due to Faraday, and in themselves contain the concept of motion. The chief contribution of the later ionic theory consisted in devising methods which made it possible to determine the number of carriers present in an electrolytic solution. Whether or not these methods, in fact, give us a true measure of the number of ions present under various conditions in no wise affects the correctness of the more general conceptions upon which the ionic theory is based.

2. *Concentration Changes Accompanying the Current: Hittorf's Numbers.* The concentration changes in the neighborhood of the electrodes were first investigated by Hittorf.[12] The fundamental conception

[11] Faraday, "Experimental Researches," Vol. 1.
[12] Hittorf, *Pogg. Ann.* *89*, 177 (1853).

underlying these concentration changes is that, within the solution, the electric current is carried by positive and negative carriers which move with velocities proportional to the potential gradient existing in the solution. Within the body of the electrolyte itself, Ohm's law is obeyed. The observed concentration change at an electrode is thus the resultant of two effects; namely, loss or gain due to the reaction at the electrode and loss or gain due to the motion of the positively and negatively charged carriers. The simplest case is that in which precipitation of the ions takes place at the electrodes. Let us assume that the charge u is transported through the solution by the cation and the charge v by the anion. Then $\frac{u}{u+v}$ will be the fraction of the charge carried by the positive ion and $\frac{v}{u+v}$ the fraction of the charge carried by the negative ion. If one equivalent of material is precipitated at the cathode, then u and v will represent the number of equivalents of matter carried up to the electrodes as cation and anion respectively. The concentration change in the neighborhood of the cathode will correspond to a loss of one equivalent of the electrolyte due to precipitation at the electrode and to a gain of $\frac{u}{u+v}$ equivalents carried up to the electrode by the cations. The total observed concentration change, therefore, will be equal to the difference of these two or to a loss of $\frac{v}{u+v}$ equivalents. Similarly, at the anode, the change will correspond to $\frac{u}{u+v}$ equivalents. It is evident that, if the concentration change due to the passage of a given charge is known and if the nature of the electrode reactions is known, then the ratios $\frac{v}{u+v}$ and $\frac{u}{u+v}$ may be determined. These ratios, which Hittorf termed the "transference numbers" of the cation and anion, respectively, we shall denote by the symbols n and $1 - n$.

In determining the transference numbers of an electrolyte by the method of Hittorf, the concentration changes are measured with respect to water. In other words, the determination of these numbers is based upon the assumption that water itself remains at rest, and is in no wise concerned in the process of the transfer of electricity through the solution. We now know that this condition is not strictly fulfilled and that water plays a part in the conduction process. When a current of electricity passes through an aqueous solution, the solvent itself is transferred to some extent along with the ions. Obviously, this will affect the concen-

tration changes observed at the electrodes. In order to determine the relative amounts of solvent transferred by the two ions, it is necessary that there should be present in the solution some reference substance which remains at rest when the current passes through the solution. The concentration changes may then be referred to this reference substance and the true transference numbers of the electrolyte determined, together with the relative amounts of water associated with the transfer of the charge through the solution. Since the results of such measurements will be discussed in detail in another chapter, it will be unnecessary to proceed further with their discussion here. They have been alluded to at this point merely for the purpose of calling attention to the fundamental assumption underlying the Hittorf method of determining transference numbers.

That the passage of the current through an electrolyte is accompanied by a transfer of matter may also be shown by other means, as, for example, by introducing a surface of discontinuity [13] in the path of a conducting electrolyte. Such surfaces of discontinuity may be observed visually and thus yield a very direct method for demonstrating the transfer of matter by means of the current within the body of the electrolyte. If, for example, a solution containing hydrochloric acid is superimposed on a solution containing potassium chloride and a current is passed through the boundary of these solutions in such direction that the more rapidly moving ion, namely, in this case, the hydrogen ion, precedes the more slowly moving ion, the potassium ion, then the boundary between the two solutions will advance in the direction of the positive current. The rate of motion of the boundary under a given potential gradient will depend upon the speed of the carriers. If a solution of an electrolyte is placed between solutions of two other electrolytes, each of which has one ion in common with the first, then, under the action of a potential, the two boundaries will move in opposite directions, the boundary between the cations moving toward the cathode and that between the anions toward the anode. It is of course necessary that the conditions for stability of the boundaries should be fulfilled. This requires that at each boundary the more rapidly moving ion shall move in advance of the more slowly moving ion. Allowing for certain corrections which must be made, the ratio of the speeds of the two boundaries is proportional to the current carrying capacities of the two ions.[14]

While the method of moving boundaries may thus be employed for measuring the transference numbers of electrolytes, its chief value, per-

[13] Lodge, *Brit. Ass. Reports*, p. 389 (1886).
[14] Lewis, *J. Am. Chem. Soc.* 32, 863 (1910).

haps, lies in that it enables us to observe the motion of the electrolyte within the solution visually.

The results of transference measurements cannot be interpreted without a knowledge of the nature of the ions within the solution. The transference numbers are calculated from the observed concentration changes on an assumption as to the nature of the ions themselves. For example, in determining the transference numbers of potassium chloride by the Hittorf method, it is assumed that only potassium is transferred to the cathode and chlorine to the anode. If, however, ions different from those assumed exist in the solution, these will take part in the transfer of electricity and will have an influence upon the observed concentration changes at the electrodes. The question as to whether or not the ions have the simple structure commonly assumed is one which ultimately must be answered on the basis of considerations derived from other properties of these solutions. That complex ions are formed in the case of certain solutions was conclusively shown by Hittorf.[15] He found that in solutions of cadmium iodide the transference number of the cation, as measured, is greater than unity. Since this ion cannot transport more current than the total passing through the solution, it is obvious, as Hittorf pointed out, that the result may be accounted for by assuming that complex cations are formed by means of which iodine is transferred from the anode to the cathode. The effect of this is to lessen the concentration increase of iodine in the neighborhood of the anode due to the transfer of the iodide ion.

If either positive or negative ions of more than one kind occur in solution, an equilibrium must exist among them by virtue of which the relative concentration of these ions will be a function of the total concentration of the salt. In general, with decrease in concentration, the more complex ions break up into simpler ones. It follows, therefore, that if complex ions exist in solution, the transference numbers should vary as a function of the concentration.

We may now examine the numerical values of the transference numbers which have been determined for various electrolytes and which are given in Table I.[16] At a concentration of 5 millimols per liter, the cation transference number for sodium chloride, for example, is 0.396. Correspondingly, the anion transference number is 0.604. This means that in a sodium chloride solution of this concentration the fraction 0.396 of the current is carried by positively charged carriers, and the remainder by negatively charged carriers. It will be observed that, in general, the

[15] Hittorf, *loc. cit.*
[16] Noyes and Falk, *J. Am. Chem. Soc.* 33, 1436 (1911).

TABLE I.

CATION TRANSFERENCE NUMBERS ($\times 10^3$) OF VARIOUS ELECTROLYTES IN WATER AT OR NEAR 18°.

Electrolyte	Temp.	Concentration 0.005	0.01	0.02	0.05	0.1	0.2	0.3	0.5	1.0
NaCl	18°	396	396	396	395	393	390	388	382	369
KCl	18	496	496	496	496	495	494	...	...	...
LiCl	18	...	332	328	320	313	304	299	...	...
NH_4Cl	18	...	492	492	492	...	...	...	...	...
NaBr	18	395	395	395	...	...	...	...	...	...
KBr	18	...	495	495	...	...	...	...	...	...
$AgNO_3$	18	...	471	471	471	471	...	...	...	...
HCl	18	832	833	833	834	835	837	838	840	844
HNO_3	20	839	840	841	844	...	...	...	...	...
$BaCl_2$	16	...	...	...	...	420	408	401	391	...
$CaCl_2$	20	440	432	424	413	404	395	389	...	...
$SrCl_2$	20	...	441	435	427	...	...	...	...	...
$CdCl_2$	18	430	430	430	430	430	...	...	...	...
$CdBr_2$	18	430	430	430	430	429	410	389	350	222
CdI_2	18	445	444	442	396	296	127	46	3	...
Na_2SO_4	18	...	392	390	383	...	...	...	...	...
K_2SO_4	18	...	494	492	490	...	...	...	...	...
Tl_2SO_4	25	...	...	...	478	476	...	...	...	...
H_2SO_4	20	...	...	822	822	822	820	818	816	812
$Ba(NO_3)_2$	25	...	...	...	456	456	456	...	...	...
$Pb(NO_3)_2$	25	...	...	...	487	487	...	...	...	...
$MgSO_4$	18	388	385	381	373	...	...	...	...	...
$CdSO_4$	18	...	389	384	374	364	350	340	323	294
$CuSO_4$	18	...	...	375	375	373	361	348	327	...

transference numbers are functions of the concentration. This concentration effect is much more pronounced in concentrated than in dilute solutions, where these numbers appear to approach limiting values. If the underlying assumptions are correct and if complex ions are not present in solutions of these electrolytes, then the change in the transference numbers at higher concentrations indicates a change in the relative speed of these ions. In general, at higher concentrations the transference number of the more slowly moving ion decreases. A portion of the effect at higher concentrations may be due to a transfer of water with the ions. But this is not sufficient to account for the entire change in the transference numbers. In most cases, the change in the transference numbers does not become pronounced until concentrations are reached where the viscosity of the solution is materially affected by the electrolyte. Since the motion of a particle through a viscous medium

is a function of its viscosity, it may be inferred that in part, at least, the variation in the transference numbers at the higher concentrations is due to the change of the viscosity of the solution.

It will be observed that the transference numbers for potassium chloride are very nearly 0.5. In other words, in the case of this salt, each ion carries very nearly one half of the current. If the frictional resistance, which an ion meets in its motion through the medium, is independent of the sign of its charge, then this indicates that the two ions have approximately the same dimensions. This is borne out by the measurements of Washburn [16a] who showed that these ions are hydrated to approximately the same extent.

The transference numbers of electrolytes are functions of the temperature. In Table II [17] are given the transference numbers of a number

TABLE II.

CATION TRANSFERENCE NUMBERS ($\times 10^3$) OF VARIOUS ELECTROLYTES AS FUNCTIONS OF THE TEMPERATURE.

Temp.	NaCl	KCl	HCl	$BaCl_2$
0°	387	493	845	437
10	...	495	841	441
18	397	496	833	...
30	404	498	823	444
50	...	...	801	475
96	...	...	748	...

of electrolytes at temperatures from 0° to 96° at concentrations in the neighborhood of 0.015 N. In the case of potassium chloride, the transference number varies only very little with the temperature, whereas in that of sodium chloride the transference number of the cation increases, and in that of hydrochloric acid it decreases. As we shall see later, it is a general rule that with increase of temperature the transference numbers of all electrolytes approach the value 0.5. The transference numbers of ions having values greater than 0.5, therefore, decrease with increasing temperature; and those having smaller values increase under the same conditions.

3. *The Conductance of Electrolytic Solutions.* The conductance of an electrolytic solution is a function of the various factors which determine its condition, such as concentration, temperature, etc. The quantity actually measured is the specific conductance of the solution. This is defined as the conductance in reciprocal ohms of a column of electro-

[16a] Washburn, *J. Am. Chem. Soc. 31,* 322 (1909).
[17] Noyes and Falk, *loc. cit.*

lyte having a cross-section of 1 sq. cm. and a length of 1 cm. The specific conductance is a function of concentration, increasing, in general, with increasing concentration. However, in the case of certain electrolytes at very high concentrations, the specific conductance passes through a maximum. This is the case, for example, with sulphuric and hydrochloric acids dissolved in water, as well as with certain other electrolytic solutions.

The specific conductance, however, is a quantity which is not well adapted to the purpose of comparing the conductance of different electrolytes. In the case of this property, as in that of many others, it is advantageous to refer the numerical values to equivalent amounts of the dissolved electrolyte. If, therefore, the conductance of a given electrolyte at two given concentrations is to be compared, the specific conductance is divided by the equivalent concentration. This quantity is called the equivalent conductance. As stated above, the specific conductance is referred to a unit cube of the electrolyte; that is, to a cube having a length of 1 cm. and a cross-section of 1 sq. cm. In order to avoid unnecessary factors in the expression for the equivalent conductance, it is desirable to express the concentration of the electrolyte in equivalents per cubic centimeter, rather than in equivalents per liter.[18] In what follows we shall employ the Greek letter η to express the concentration in equivalents per c.c., while the letter C will be employed to express the concentration in equivalents per liter. We have therefore $1000\eta = C$. If we represent the equivalent conductance by the Greek letter Λ, and the specific conductance by the Greek letter μ, then we obviously have:

(1) $$\Lambda = \frac{\mu}{\eta} = \frac{1000\mu}{C}$$

The value of the equivalent conductance Λ measures, in fact, the conducting power of the electrolyte in a solution of a given concentration. Suppose, for example, that one equivalent of electrolyte were contained between two electrodes 1 cm. wide, separated by 1 cm., and of indefinite extent vertically. If the entire electrolyte were contained in 1 cu. cm. of liquid, then the equivalent conductance would obviously be equal to the specific conductance at this concentration, which is unity. If, now, more solvent were added to this solution, the amount of solute remaining constant, the concentration of the solution would be decreased. At the same time there would be an increase in the electrode area, but the total amount of conducting material between the electrodes and the

[18] Kohlrausch and Holborn, "Leitvermögen der Elektrolyte," 1898, p. 84.

TABLE III.

EQUIVALENT CONDUCTANCES OF ELECTROLYTES IN WATER AT 18° AT VARIOUS CONCENTRATIONS.

Concentration C.	0	10^{-4}	2×10^{-4}	5×10^{-4}	10^{-3}	2×10^{-3}	5×10^{-3}	10^{-2}	2×10^{-2}	5×10^{-2}	10^{-1}	2×10^{-1}	5×10^{-1}	1
$NaCl$	108.9	108.03	107.75	107.11	106.42	105.48	103.71	101.88	99.55	95.66	91.96	87.67	80.89	74.31
KCl	130.0	129.00	128.70	128.04	127.27	126.24	124.34	122.37	119.90	115.69	111.97	107.90	102.36	98.22
$LiCl$	98.8	97.96	97.67	97.01	96.34	95.44	93.75	91.97	89.75	85.97	82.28	77.80	70.60	63.27
$RbCl$	133.0	132.3	....	....	130.3	....	....	125.3	....	....	113.9	....	....	101.9
$CsCl$	133.5	132.2	131.9	131.24	130.54	129.38	127.33	125.07	....	....	113.44	....	....	....
$TlCl$	131.4	130.33	130.00	129.18	128.23	126.81	123.73	120.21	....	....	....	....	....	....
NH_4Cl	130.2	....	....	....	....	126.5	....	122.5	118.1	....	....	....	....	....
KBr	132.2	131.05	130.76	130.05	129.28	128.22	126.31	124.31	121.78	117.69	114.14	110.32	105.30	....
KI	131.1	129.76	129.50	128.97	128.25	127.21	125.33	123.44	121.10	117.26	113.98	....	106.2	103.60
$KSCN$	121.2	120.13	119.93	119.29	118.55	117.57	115.73	113.87	111.51	107.67	104.21	....	95.63	91.55
KF	111.2	110.37	110.13	109.48	108.80	107.82	106.07	104.19	101.78	97.65	93.94	....	82.0	75.95
NaF	90.1	89.24	88.95	88.39	87.76	86.89	85.17	83.38	81.0	76.94	73.06	67.9	59.9	51.9
TlF	112.6	114.38	114.64	114.45	113.25	111.29	108.18	105.44	102.22	97.38	92.61	....	78.78	71.54
$NaNO_3$	105.2	104.45	104.09	103.53	102.75	101.80	99.97	98.07	95.57	91.35	87.16	82.21	73.99	65.81
KNO_3	126.3	125.40	125.08	124.34	123.55	122.50	120.38	118.10	115.12	109.78	104.71	98.67	89.18	80.41
$LiNO_3$	95.1	94.30	93.99	93.36	92.71	91.81	90.18	88.46	86.27	82.58	79.06	74.89	67.88	60.69
$TlNO_3$	127.7	126.63	126.30	125.61	124.70	123.48	121.11	118.38	....	107.93	101.19	....	....	....
$AgNO_3$	115.8	115.01	114.56	113.88	113.14	112.07	110.03	107.80	105.1	99.50	94.33	....	77.5	67.6
$KClO_3$	119.6	118.63	118.35	117.68	116.92	115.84	113.84	111.64	108.81	103.74	99.19	93.73	85.28	....
$KBrO_3$	112.1	....	....	....	109.9	108.7	106.9	104.7	102.0	97.3	93.0	87.8	....	....
$NaIO_3$	77.4	76.69	76.44	75.83	75.19	74.30	72.62	70.86	68.56	64.43	60.46	55.45	....	....
KIO_3	98.5	97.64	97.34	96.72	96.04	95.04	93.2	91.24	88.64	84.06	79.67	74.34	....	....
$LiIO_3$	67.3	66.66	66.43	65.87	65.27	64.43	62.89	61.23	59.05	55.26	51.50	46.88	38.98	31.21
HCl	380.0	378.1	377.8	377.0	375.9	375.3	372.6	369.3	365.5	358.4	351.4	....	....	....
HNO_3	376.5	....	....	373.9	372.9	371.4	....	365.0	....	353.7	346.4	....	....	....
$BaCl_2$	120.9	....	....	117.01	115.60	....	....	106.67	102.53	96.04	90.78	85.18	77.29	70.14
$CaCl_2$	117.4	115.17	114.55	113.34	111.96	110.07	106.70	103.37	99.38	93.29	88.19	82.79	74.92	67.54
$MgCl_2$	111.4	109.43	108.87	107.68	106.35	104.52	101.30	98.14	94.33	88.47	83.42	77.84	69.50	61.45
$PbCl_2$	126.3	....	....	....	119.15	115.8	109.2	102.1	93.2	79.2	....	....	....	....
$CdCl_2$	111.9	....	....	....	104.2	99.7	89.9	82.2	74.2	62.1	50.1	41.0	30.4	21.4
$CdBr_2$	114.1	....	....	....	102.3	97.9	85.5	75.4	65.4	51.7	43.0	34.8	24.9	17.9
CdI_2	113.0	....	....	....	97.5	91.4	76.3	64.8	53.0	39.0	29.5	23.3	18.1	15.1
$Ba(NO_3)_2$	117.2	115.32	114.65	113.30	111.72	109.50	105.29	100.96	95.66	86.81	78.94	70.18	56.60	....
$Sr(NO_3)_2$	113.7	111.74	111.07	109.76	108.31	106.35	102.74	99.04	94.52	87.30	80.93	73.80	62.72	52.07
$Ca(NO_3)_2$	113.7	111.91	111.19	109.93	108.49	106.54	103.07	99.53	95.18	88.41	82.48	75.94	65.70	55.86

TABLE III.—*Continued.*

Concentration C	0	10^{-4}	2×10^{-4}	5×10^{-4}	10^{-3}	2×10^{-3}	5×10^{-3}	10^{-2}	2×10^{-2}	5×10^{-2}	10^{-1}	2×10^{-1}	5×10^{-1}	1
$Mg(NO_3)_2$	107.7	....	....	....	102.6	100.8	97.7	94.65	90.9	85.3	80.5	75.3	....	....
$Cd(NO_3)_2$	108.2	....	....	....	107.8	105.4	99.2	94.1	91.4	85.1	77.9	71.8	63.2	53.6
$Pb(NO_3)_2$	122.6	120.73	119.94	118.08	116.13	113.54	108.68	103.55	97.01	86.38	77.27	67.36	53.21	42.02
$Ba(BrO_3)_2$	103.0	....	....	....	97.5	95.5	91.9	88.2	83.6	....	....	....	....	....
K_2SO_4	133.0	130.7	130.0	128.5	126.9	124.6	120.3	115.8	110.3	101.9	94.9	87.7	78.4	71.6
Na_2SO_4	111.9	109.3	108.3	106.7	105.1	103.5	99.8	95.7	....	83.64	77.07	69.95	....	....
Li_2SO_4	101.8	....	....	97.71	96.27	....	....	86.73	82.06	74.59	68.07	60.97	50.45	41.31
Tl_2SO_4	134.4	....	....	....	127.35	124.2	118.4	112.3	104.55	92.7	83.1	73.8	....	....
Ag_2SO_4	122.5	....	....	....	116.3	113.6	108.4	102.9	96.1	....	....	....	....	....
$K_2C_2O_4$	127.5	125.09	124.83	123.82	122.43	120.46	116.73	112.83	108.07	100.77	94.79	88.57	....	73.63
H_2SO_4	....	....	....	....	....	....	....	309.0	....	253.5	233.3	....	....	....
$MgSO_4$	114.4	109.90	108.07	104.21	99.89	94.14	84.53	76.21	67.68	56.92	49.68	43.19	....	28.91
$ZnSO_4$	115.5	109.7	107.7	103.5	98.6	92.2	81.9	72.9	63.8	52.8	45.4	39.1	....	26.2
$CdSO_4$	114.9	109.84	107.60	102.93	97.72	90.92	79.70	70.34	60.95	49.60	42.21	35.89	28.74	23.58
$CuSO_4$	114.4	109.95	107.95	103.56	98.56	91.94	80.98	71.74	62.40	51.16	43.85	37.66	....	25.77
MgC_2O_4	109.0	94.5	87.0	74.5	63.4	51.4	38.2	29.6	23.0	16.4	12.7	10.0	....	....
$K_4Fe(CN)_6$	159.5	....	....	....	....	137.0	....	113.4	....	93.7	84.9	77.8	....	....
$Ca_2Fe(CN)_6$	147.0	....	....	....	....	75.5	....	49.9	....	38.5	35.1	32.9	....	....
$La(NO_3)_3$	122.8	....	....	....	....	110.8	....	98.5	....	86.1	79.4	72.1	....	....
$La_2(SO_4)_3$	129.5	....	....	....	....	60.1	....	37.4	....	25.7	21.4	17.8	....	....
$K_3C_6H_5O_7$	124.6	....	....	120.1	....	115.4	109.9	101.8	....	87.8	80.8	....	....	....

average distance which the conducting particles would have to travel between these electrodes would remain fixed. If the cell were filled to a height of l centimeters and if the conductance of the solution between the pair of electrodes were Λ, then, since the electrode area is equal to the reciprocal of the concentration, i.e., to $1/l$, it follows that the specific conductance of this solution would be:

$$\mu = \frac{\Lambda}{l} = \Lambda\eta$$

Therefore, in order to compare the conducting power of a solution of a given electrolyte at different concentrations, we divide the specific conductance of the solution by the concentration and compare the values of this ratio, namely the values of Λ. Similarly, in comparing the conducting power of solutions of different electrolytes in the same or different solvents at the same concentration, the values of the equivalent conductance of the electrolytes at that concentration are obviously to be compared. The equivalent conductance is a measure of the conducting of an equivalent amount of material. In comparing the conducting power of solutions, therefore, we require the values of the equivalent conductance Λ for these solutions.

Values of the equivalent conductance of typical electrolytes in water at 18° are given in Table III.[19] The concentrations in this case are expressed in equivalents per liter. It will be observed that as the concentration of an electrolyte in water decreases, its equivalent conductance increases. For a decrease in the concentration in the ratio of one to two between normal and half normal, the equivalent conductance of a binary electrolyte increases approximately 30%. For a corresponding decrease in concentration between 1 and 0.5 milli-equivalent per liter, the equivalent conductance increases less than 1%. It is apparent, therefore, that as the concentration decreases, the equivalent conductance approaches a limiting value.

The relation between the equivalent conductance and the concentration is shown graphically in Figure 1, where values of the equivalent conductance of aqueous solutions of KCl, NaCl and $LiIO_3$ are plotted as ordinates and the logarithms of the concentrations as abscissas. The curves for different electrolytes are evidently similar in form. As the concentration decreases, the equivalent conductance apparently approaches a definite value as a limit. A curve of this type, however, does not lend itself to a determination of the limiting value which the conductance approaches as the concentration decreases indefinitely. For

[19] Noyes and Falk, *J. Am. Chem. Soc.* 34, 454 (1912).

the purposes of graphical extrapolation it is preferable to employ some function of the concentration which brings the point of zero concentration, to which the extrapolation must be carried, to one of the axes on the plot. A convenient function which yields a simple type of curve is the cube root of the concentration. Such plots for potassium chloride and sodium chloride are shown in Figure 2. If the curves for potassium chloride and sodium chloride are extrapolated, they yield for the limiting value of the equivalent conductance values in the neighborhood of 130.0 and 108.9 respectively. The value obtained for Λ_0 will, of course, depend upon the extrapolation function employed. In another chapter

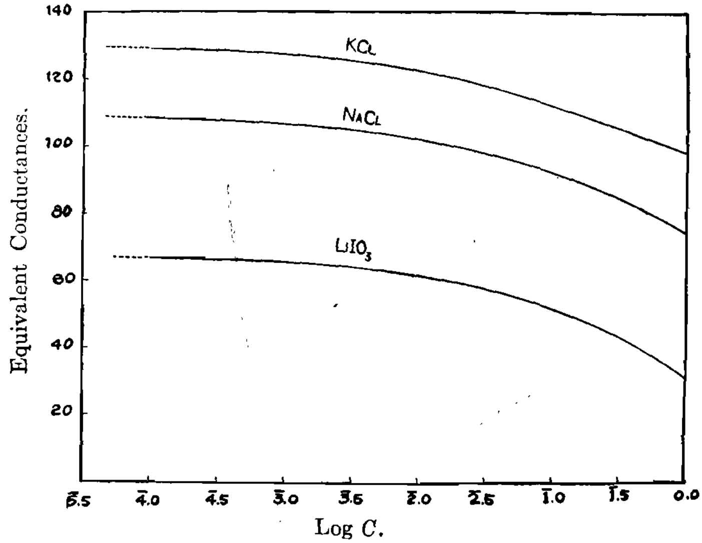

Fig. 1. Showing Λ as a Function of Log C for Aqueous Solutions at 18°.

various functions proposed for this purpose will be discussed more in detail. For the present it will be sufficient to employ approximate values for the purpose of comparing the behavior of different electrolytes.

The equivalent conductance of hydrochloric acid is much greater than that of the salts. The conductance curve, however, is similar in form to that of the salts. That is, with decreasing concentration, the equivalent conductance approaches a *limiting* value. In the case of hydrochloric acid this value is in the neighborhood of 380 at 18°. We may now ask the question: To what are the differences in the values of the equivalent conductance of the different electrolytes due? Why, for example, is the equivalent conductance of hydrochloric acid greater than that of potassium chloride? Or, in other words, to what is the greater

conductance of hydrochloric acid due? It will be recalled that at a temperature of 18° and a concentration of 0.01 normal, for example, the value of the transference numbers of the positive ions in sodium chloride, potassium chloride and hydrochloric acid are 0.396, 0.496 and 0.833 respectively. In the case of these electrolytes the negative carrier

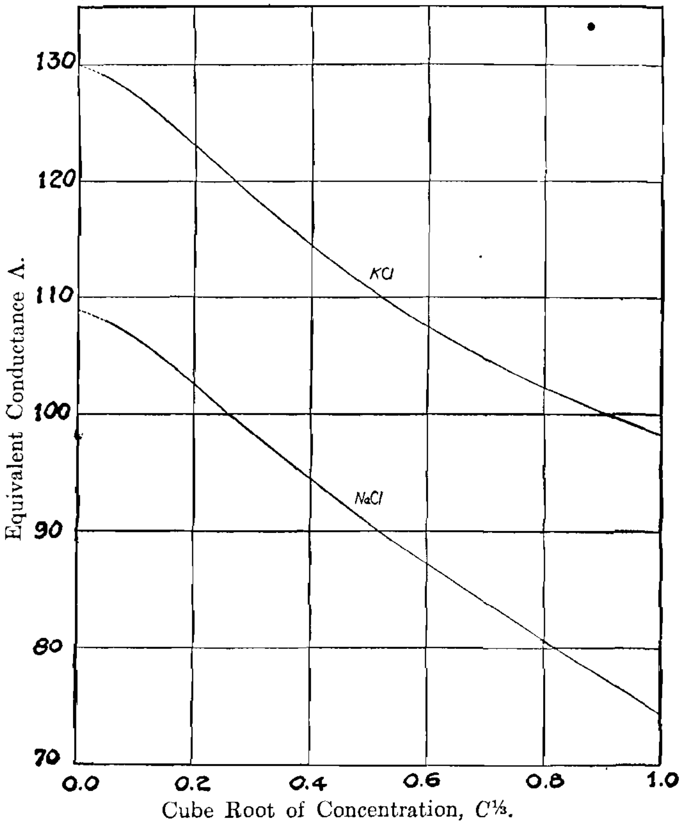

FIG. 2. Showing Λ as a Function of $C^{1/3}$.

is presumably the same, namely, the chloride ion, and it is only the positive carriers which differ in these electrolytes. If, then, the negative carriers are the same in solutions of these electrolytes, it may be assumed that the current carried by these carriers in these solutions under the same conditions of temperature and concentration will be approximately the same, and consequently the difference in the conducting power of these electrolytes is due to the difference in the conducting power of their positive carriers. The carrying capacities of the sodium, potassium

and the hydrogen ions are, therefore, 0.656, 0.984 and 1.972 times that of the chloride ion respectively. In other words, the carrying capacity of the hydrogen ion is 3 times that of the sodium ion and 2 times that of the potassium ion. If the tables of the conductance and of the transference numbers are compared, it will be seen that in the more dilute solutions it is generally true that, for salts having an ion in common, those salts whose ions have greater transference numbers likewise have greater conducting power.

We now come to an important generalization due to Kohlrausch,[20] namely: In a solution of a single electrolyte, the two ions move independently of each other. Therefore, we may determine the fraction of the current carried by each ion, or, in other words, the conductance of each ion in a given solution, by multiplying the equivalent conductance of the solution by the transference number of the electrolyte in this solution. If this is true, then, in a solution of sodium chloride having a concentration of 0.01 normal at 18°, the conductance due to the sodium ion is $101.88 \times 0.396 = \Lambda_{Na} = 40.34$. Similarly, the conductance of the potassium and hydrogen ions under the same conditions is:

$$\Lambda_K = 122.37 \times 0.496 = 60.69$$

$$\text{and } \Lambda_H = 369.3 \times 0.833 = 307.63$$

In these solutions the conductance of the chloride ion is 61.54, 61.68 and 61.67 for NaCl, KCl and HCl respectively. The conductance of the chloride ion is thus very nearly the same in equivalent solutions of these electrolytes. It is, however, by no means certain that the conductance of a given ion will in all cases be the same in solutions of different salts. If the transference numbers of an electrolyte are known at a given concentration, then the conductance of its ions may be calculated.

4. *Ionization of Electrolytes.* As we have seen, the equivalent conductance of a solution, which measures, so to speak, the conducting power of the dissolved electrolyte under given conditions, increases with decreasing concentration and appears to approach a limiting value. The current passing through an electrolyte under given conditions is carried, in the case of the simpler types of salts, by two charged constituents, namely the positive and the negative carriers, which, according to Faraday, are termed the cation and the anion respectively. The relative amounts of the current carried by the positive and negative ions may be determined by means of transference experiments, which depend ultimately upon the concentration changes produced by the motion of the

[20] Göttinger, "Nachrichten," 1876, p. 213.

carriers. If the current in a solution of an electrolyte is effected through the motion of charged carriers within the electrolyte, then we may inquire: What fraction of the electrolyte present in the solution is concerned in the process of conduction; that is, what fraction of the electrolyte exists in an ionic condition?

Clausius[21] suggested that electrolytes are ionized, but he failed to draw any definite conclusion as to the extent of this ionization. In his time, the notion that a stable compound, such as potassium chloride, could be dissociated and moreover dissociated into oppositely charged constituents was contrary to accepted theories. Clausius was therefore content to merely throw out the suggestion that electrolytes are to some extent dissociated.

The conclusion that an electrolyte is dissociated follows almost necessarily from the work of Kohlrausch and Hittorf, although neither of these investigators actually drew this conclusion. It was Arrhenius[22] who proposed the fundamental hypothesis that an electrolyte in solution is dissociated and that the degree of its dissociation may be determined by means of the conductance of its solutions. Moreover, he showed that the dissociation as measured in this way is in agreement with many other well-known properties of these solutions.

We have seen that, as the concentration of a solution decreases, its equivalent conductance increases and approaches a limiting value. We have also seen that the positive and negative ions within the electrolyte appear to move at definite rates under fixed conditions, provided the concentration of the solution is not too great, and that the motion of the ions under these conditions takes place independently for each ion. If these conclusions are correct, then it appears that a logical explanation of the facts would be that, in the more concentrated solutions, a portion of the electrolyte has been removed from a condition in which it is able to take part in the conduction process, while the fraction of the substance which remains in a conducting condition is measured by the ratio of the conductance at a given concentration to the conductance at very low concentrations, where apparently all the electrolyte takes part in the conduction process.

Let γ represent the fraction of the salt present in a conducting state; then the relative amount of the salt present in this state at any concentration will be given by the ratio:

$$\gamma = \frac{\Lambda}{\Lambda_0}, \qquad (2)$$

[21] Clausius, *Pogg. Ann.* *101*, 338 (1857).

[22] Arrhenius, *Bijhanj till K. Svenska, Vet. Akad. Handl.* No. 13, 1884; Sixth Circular of the British Association Committee for Electrolysis, May, 1887; *Ztschr. f. phys. Chem.* *1*, 631 (1887).

where Λ is the equivalent conductance of the solution at the concentration C, and Λ_0 is the limiting value which the conductance approaches as the concentration decreases without limit. According to this theory, we may calculate the fraction of electrolyte in an ionized condition, if we know the equivalent conductance and the limiting value which the equivalent conductance approaches at zero concentration. In Table III were given values of the equivalent conductance of a number of electrolytes at a series of concentrations. The approximate limiting values Λ_0, which the equivalent conductance approaches at low concentrations, appear in the second column of that table. From these values we may calculate the degree of ionization of the electrolytes at any concentration falling within the intervals given. In the case of potassium chloride, for example, $\Lambda_0 = 130.0$, approximately, and the equivalent conductance at normal concentration is 98.22. Therefore, the ionization of potassium chloride at this concentration is approximately 75%; that is, of the total potassium chloride present in solution at this concentration, 75% is concerned in the actual process of conduction and 25% takes no part in this process.

The ionization values of various electrolytes in water at 18° are given in Table IV.[23] It will be observed that the ionization of salts of the

TABLE IV.

IONIZATION VALUES OF ELECTROLYTES IN WATER AT 18°.

Concentration, C.	10^{-3}	2×10^{-3}	5×10^{-3}	10^{-2}	2×10^{-2}	5×10^{-2}	10^{-1}	2×10^{-1}	5×10^{-1}	1.0
NaCl	.977	.969	.953	.936	.916	.882	.852	.818	.773	.741
KCl	.979	.971	.956	.941	.922	.889	.860	.827	.779	.742
LiCl	.975	.966	.949	.932	.911	.878	.846	.812	.766	.737
RbCl	.980	....	....	.942	....	....	.855	....	....	.748
CsCl	.978	.969	.954	.937	....	....	.847	....	....	....
TlCl	.976	.965	.942	.915	....	....	....	....	....	....
KBr	.978	.970	.955	.940	.921	.888	.859	.825	.766	....
KI	.978	.970	.956	.941	.922	.890	.869	....	.773	.727
KSCN	.978	.970	.955	.940	.920	.888	.860	....	....	....
KF	.978	.970	.954	.937	.915	.878	....	....	....	....
NaF	.974	.964	.945	.925	.899	.854	....	....	....	....
TlF	....	....	.961	.936	.908	.865	....	....	....	....
$NaNO_3$	.977	.968	.950	.932	.910	.871	.832	.788	.719	.660

[23] Noyes and Falk, *J. Am. Chem. Soc.* *34*, 454 (1912).
In calculating the ionization at the higher concentrations Noyes and Falk have corrected for the viscosity change of the solution due to the added electrolyte. While there is every reason for believing that the change in the viscosity of the solution entails a change in the speed of the carriers, in general, the change in speed is probably not directly proportional to the change in the fluidity of the medium. All ionization values at higher concentrations, therefore, are more or less in doubt. As a rule the viscosity effects are small at concentrations below 10^{-2} N. In comparing the ionization of various electrolytes, therefore, it is best to choose concentrations at which the viscosity effect may be neglected.

TABLE IV.—*Continued*

Concentration, C.	10^{-3}	2×10^{-3}	5×10^{-3}	10^{-2}	2×10^{-2}	5×10^{-2}	10^{-1}	2×10^{-1}	5×10^{-1}	1.0
KNO_3	.978	.970	.953	.935	.911	.867	.824	.772	.688	.613
$LiNO_3$	.975	.965	.950	.932	.911	.874	.840	.803	.750	.703
$TlNO_3$	.977	.967	.948	.926	....	.843	.788	....	....	....
$AgNO_3$	.977	.968	.950	.931	.908	.859	.814	....	.683	.617
$KBrO_3$	.980	.970	.954	.934	.910	.868	.830	....	....	....
$KClO_3$	.978	.969	.952	.933	.910	.866	.827	.780	.703	....
$NaIO_3$	.971	.960	.939	.917	.890	.842	.801	.752	....	....
KIO_3	.975	.965	.946	.928	.903	.860	.819	.775	....	....
$LiIO_3$	.970	.958	.936	.912	.883	.834	.789	.740	.682	.643
HCl	.990	.988	.981	.972	.962	.944	.925	....	....	....
HNO_3	.992	.987	....	.970	....	.940	.921	....	....	....
$BaCl_2$	.956	....	....	.883	.850	.798	.759	.720	.672	.642
$CaCl_2$	.954	.938	.910	.882	.849	.802	.764	.727	.686	.662
$MgCl_2$	.955	.939	.910	.883	.851	.803	.765	.728	.687	.669
$PbCl_2$	.943	.917	.865	.808	.738	.627	....	....	....	....
$CdCl_2$	.931	.891	.803	.735	.664	.559	.453	.375	.289	.217
$CdBr_2$	*.897*	*.858*	*.749*	*.661*	*.573*	....	....	....	....	....
CdI_2	.870	.809	.675	.573	.469	....	....	....	....	....
$Ba(NO_3)_2$	.953	.934	.898	.861	.818	.744	.679	.609	.504	....
$Sr(NO_3)_2$	.953	.935	.904	.871	.833	.770	.719	.661	.579	.511
$Ca(NO_3)_2$	.954	.937	.907	.876	.838	.781	.731	.679	.609	.549
$Mg(NO_3)_2$	.953	.936	.907	.880	.847	.799	.760	.721	....	....
$Pb(NO_3)_2$	.947	.926	.886	.845	.793	.708	.635	.559	.454	.377
$Cd(NO_3)_2$	.996	.974	.917	.871	.848	.792	.731	.684	.628	.577
$Ba(BrO_3)_2$	.947	.927	.892	.856	.812	....	....	....	....	....
K_2SO_4	.954	.937	.905	.872	.832	.771	.722	.673	.618	.592
Na_2SO_4	.939	.925	.893	.857	....	.756	.704	.652	....	....
$LiSO_4$	.946	....	....	.854	.811	.744	.688	.633	.567	.528
Tl_2SO_4	.948	.924	.882	.837	.780	.694	.625	.561	....	....
Ag_2SO_4	.949	.927	.885	.840	.784	....	....	....	....	....
$K_2C_2O_4$	.960	.945	.916	.886	.849	.795	.753	.711	....	.643
$MgSO_4$	.873	.823	.740	.669	.596	.506	.449	.403	....	.349
$ZnSO_4$	.854	.799	.710	.633	.556	.464	.405	.360	....	.309
$CdSO_4$	.850	.791	.694	.614	.534	.437	.377	.332	.290	.277
$CuSO_4$	.862	.804	.709	.629	.550	.455	.396	.351	....	.309
MgC_2O_4	.582	.472	.350	....	....	....	....	....	....	....
$K_4Fe(CN)_6$	....	.859	....	.712	....	.591	.538	.498	....	....
$La(NO_3)_3$	....	.902	....	.802	....	.701	....	....	....	....
$K_3C_6H_5O_7$	....	.926	.882	.817	....	.705	....	....	....	....
$La_2(SO_4)_3$	....	.464	....	.289	....	.198	....	....	....	....
$Ca_2Fe(CN)_6$	....	.514	....	.339	....	.262	....	....	....	....

same type is approximately the same at the same concentration. This is particularly true at the lower concentrations where the divergence in many cases is scarcely greater than the experimental error. The strong

acids and bases, however, have a markedly higher ionization than the salts. Salts of higher type exhibit a lower degree of ionization than simpler salts. But here, again, salts of the same type have approximately the same ionization at corresponding concentrations.

If electrolytes approach complete ionization at low concentrations and if the ions in these solutions move independently of one another, then, if the transference numbers of the electrolytes are known, the value of the equivalent conductance of the individual ions may be calculated. If the conductances of a sufficient number of pairs of electrolytes have been determined, it is only necessary to know the transference number of a single electrolyte. In general, the values of the ionic conductances are based upon the transference number of potassium chloride. The values of the equivalent conductances of various ions in water at 18° are given in Table V.[24]

TABLE V.

EQUIVALENT CONDUCTANCES OF THE INDIVIDUAL IONS AT 18°.

Cs	68.0	Ba	55.4	Cl	65.5
Rb	67.5	Ca	51.9	NO_3	61.8
Tl	65.9	Sr	51.9	SCN	56.7
NH_4	64.7	Zn	47.0	ClO_3	55.1
K	64.5	Cd	46.4	BrO_3	47.6
Ag	54.0	Mg	45.9	F	46.7
Na	43.4	Cu	45.9	IO_3	34.0
Li	33.3	La	61.0	SO_4	68.5
H	314.5	Br	67.7	C_2O_4	63.0
Pb	60.8	I	66.6	$Fe(CN)_6$	95.0

The equivalent conductance values of the different ions are of the same order of magnitude, although the values for the hydrogen and hydroxyl ions are markedly greater than for the other ions. This is in agreement with the greater values of the conductance of solutions of the strong acids and bases. The conductance values of the different ions appear to bear no simple relation to their constitution. So, for example, lithium, which is lighter and has a smaller atomic volume than the remaining alkali metals, has the lowest conductance of any of the ions whose conductance values are tabulated. On the other hand, the nitrate and the chloride ions have markedly higher values than the fluoride ion.

5. *Molecular Weight of Electrolytes in Solution.* The hypothesis of Arrhenius, that the ionization of an electrolyte may be measured by the

[24] Noyes and Falk, *loc. cit.*

ratio of the equivalent conductance at any concentration to the limiting value of the equivalent conductance at low concentrations, is supported by other important properties of these solutions. Raoult [25] had observed that the freezing point depression produced by electrolytes in water is greater than that of other substances at equivalent concentrations. van't Hoff,[26] finally, supplied the theoretical foundation which made it possible to calculate from the measurements of Raoult the molecular weight of substances in solution. Since in the case of aqueous salt solutions the depression was found to be abnormal, van't Hoff introduced an arbitrary factor i, which he apparently assumed to be a constant independent of concentration. Arrhenius at once recognized the significance of van't Hoff's factor and pointed out the relation between this factor and the coefficients derived from conductance measurements. According to Arrhenius, if electrolytes are dissociated, the freezing point depression of their solutions as measured should be greater than that calculated according to the method of van't Hoff, the molecular weight being assumed equal to the formula weight of the dissolved substance. If we let

$$\frac{M}{M_C} = i, \tag{3}$$

where M is the formula weight and M_C the molecular weight calculated from freezing point measurements, then, obviously, there exists between i and γ, the relation:

$$i = 1 + (n - 1)\gamma, \tag{4}$$

where n is the number of ions resulting from the dissociation of a single molecule. The values of γ as calculated from freezing point or other similar determinations should thus agree with the values of γ as calculated from conductance measurements. In Table VI [27] are given the

TABLE VI.

COMPARISON OF IONIZATION VALUES DERIVED FROM CONDUCTANCE AND FROM FREEZING POINT MEASUREMENTS.

Electrolyte	Method	5×10^{-3}	10^{-2}	2×10^{-2}	5×10^{-2}	10^{-1}	2×10^{-1}	5×10^{-1}
KCl	F	.963	.943	.918	.885	.861	.833	.800
	C	.956	.941	.922	.889	.860	.827	.779
NH_4Cl	F	.947	.928	.907	.878	.856	.832	....
	C	....	.941	.921	....	....	....	....

[25] *C. R.* *94*, 1517; *95*, 188 and 1030 (1882).
[26] van't Hoff, *Sv. Vet.-Akad. Handlingar* *21*, No. 17 (1886), p. 48.
[27] Noyes and Falk, *J. Am. Chem. Soc.* *34*, 485 (1912). The concentrated solutions have been corrected for the viscosity effects. (See footnote above, p. 35.)

TABLE VI.—*Continued*

Electrolyte	Method	5×10^{-3}	10^{-2}	2×10^{-2}	5×10^{-2}	10^{-1}	2×10^{-1}	5×10^{-1}
NaCl	F	.953	.938	.922	.892	.875	.850	.824
	C	.953	.936	.916	.882	.852	.818	.773
CsCl	F	....	....	.930	.892	.863	.829	.778
	C	.954	.937	....	....	.847	....	....
LiCl	F	.944	.937	.928	.912	.901	....	....
	C	.949	.932	.890	.878	.846	.812	.766
KBr	F	....	....	.929	.889	.863	.839	.813
	C	.955	.940	.921	.888	.859	.825	.766
$NaNO_3$	F	....	.903	.885	.855	.830	.798	....
	C	.950	.932	.910	.871	.832	.788	.719
KNO_3	F	....	.901	.880	.836	.781	.711	....
	C	.953	.935	.911	.867	.824	.772	.688
$KClO_3$	F	....	.914	.891	.849	.798	....	....
	C	.952	.933	.910	.866	.827	.780	.703
$KBrO_3$	F	....	.923	.896	.854	.805	....	....
	C	.954	.934	.910	.868	....	....	....
KIO_3	F	.941	.913	.882	.828	.765	....	....
	C	.946	.928	.903	.860	.819	.775	....
$NaIO_3$	F	.939	.916	.890	.842	.773	....	....
	C	.939	.917	.890	.842	.801	.752	....
$KMnO_4$	F	.938	.921	.913	....	....	....	....
	C	.968	.951	.930	....	....	....	....
HCl	F	.991	.975	.957	.933	.917	....	....
	C	.981	.972	.962	.944	....	....	....
HNO_3	F	.974	.960	.942	.912	.900	.879	....
	C	....	.970	....	.940	....	....	....
$BaCl_2$	F	.899	.878	.855	.819	.788	.758	....
	C	....	.883	.850	.798	.759	.720	.672
$CaCl_2$	F	....	....	.876	.837	.815	.804	....
	C	.910	.882	.849	.802	.764	.727	.688
$MgCl_2$	F	....	....	.885	.854	.839	.833	....
	C	.910	.883	.851	.803	.765	.728	.687
$CdCl_2$	F	....	.791	.768	.690	.605	.539	....
	C	.803	.735	.664	.559	.453	.375	.289
$CdBr_2$	F	....	.780	.704	.589	.482	.367	....
	C	.749	.661	.573	....	....	....	....
CdI_2	F	....	.593	.540	.400	.225	.100	....
	C	.675	.573	.469	....	....	....	....
$Cd(NO_3)_2$	F	.948	.921	.901	.887	.884	....	....
	C	.917	.871	.848	.792	.731	.684	.628
$Ba(NO_3)_2$	F	.917	.888	.855	....	....	....	....
	C	.898	.861	.818	.744	.679	.609	.504
$Pb(NO_3)_2$	F	.890	.850	.804	.724	.649	.568	.427
	C	.886	.845	.793	.708	.635	.559	.454
K_2SO_4	F	.929	.899	.857	.785	.730	.667	.568
	C	.905	.872	.832	.771	.722	.673	.618

TABLE VI.—*Continued*

Electrolyte	Method	5×10^{-3}	10^{-2}	2×10^{-2}	5×10^{-2}	10^{-1}	2×10^{-1}	5×10^{-1}
Na_2SO_4	F	....	....	.867	.795	.736	.672	.567
	C	.893	.857	....	.756	.704	.652	....
$MgSO_4$	F	.694	.618	.536	.420	.324	.223	.084
	C	.740	.669	.596	.506	.449	.403	....
$CuSO_4$	F	.616	.545	.455	.318	....	....	....
	C	.709	.629	.550	.455	.396	.351	....
$ZnSO_4$	F	.665	.582	.489	....	....	....	....
	C	.710	.633	.556	.464	.405	.360	....
$CdSO_4$	F	.658	.569	.477	.343	....	....	....
	C	.694	.614	.534	.437	.377	.332	.290
$K_3Fe(CN)_6$	F	.894	.868	.778	....	....	....	....
	C	.869	.827	....	....	....	....	....
$K_4Fe(CN)_6$	F	....	....	....	.634	.581	.520	.425
	C	....	....	....	.591	.538	.498	....

values of γ as determined from freezing point (F) and from conductivity (C) measurements.

It will be observed that in the case of certain electrolytes the values of γ derived by the two methods correspond very closely. This is particularly true of potassium chloride where the two values correspond practically within the limit of experimental error up to concentrations as high as 0.1 normal. In the case of other salts, the divergence at higher concentrations is considerably greater. In general, however, the two values approach each other the more nearly, the lower the concentration of the solution. The correspondence between the two values is closest in the case of the binary salts. The more complex a salt, the greater is, as a rule, the divergence between the two values and the lower the concentration at which a given divergence appears.

The cause of the divergence of the ionization values as determined by the two methods is as yet uncertain. It is possible that the ionization is not correctly measured by the conductance ratio. At higher concentrations, at any rate, it is to be expected that various influences will make themselves felt, such as the effect of viscosity, as a result of which the conductance as measured will not yield a true measure of the ionization. On the other hand, the molecular weight, as determined by osmotic methods, may be expected to be in error, since the laws of dilute solutions are assumed in calculating these values. The only assurance we have that the laws of dilute solutions are applicable under given conditions is that the results obtained are in agreement with other facts relating to these solutions. When a disagreement occurs, therefore, it is

not known whether the laws of dilute solutions are inapplicable or whether some other discrepancy has arisen.

In the case of salts of higher type, and even in that of the simpler types of salts, there is always a possibility that the ionization process as assumed in calculating the ionization from conductance measurements does not correspond to the true reaction. For example, in calculating the ionization of barium chloride, it is assumed that the reaction takes place according to the equation:

$$BaCl_2 = Ba^{++} + 2Cl^-.$$

It is possible, however, that ionization may take place in several stages, an intermediate reaction of the type:

$$BaCl_2 = BaCl^+ + Cl^-$$

intervening. If an intermediate reaction of this type takes place, then it is obviously impossible to calculate the degree of ionization from conductance measurements. So far, it has proved difficult to establish the existence of intermediate ions. In general, it is to be expected that if intermediate ions exist, the transference numbers will vary markedly with the concentration. It should be noticed in this connection that those electrolytes, which exhibit the greatest divergence between the ionization values as calculated from conductance and from freezing point data, also exhibit a marked change in their transference numbers with change of concentration. In the case of sulphuric acid [28] the existence of an intermediate ion has been definitely established; and various considerations, based upon the solubility of salts in the presence of other salts, lend support to the view that intermediate ions exist in solutions of many salts of higher type.[29]

In any case, it is important to note that the values of i as determined from freezing point and from conductivity determinations apparently approach the same limit at low concentrations, and, moreover, the limits approached are in agreement with the constitution of the salts in question. So, for example, in the case of the binary electrolytes, the limit approached is 2, in that of ternary electrolytes 3, in that of quaternary salts 4, etc. No case has been observed in which the limit approached is greater than that corresponding to the constitution of the salt.

6. *Applicability of the Law of Mass Action to Electrolytic Solutions.* On their surface, the results of conductance and of freezing point measurements appear to be in substantial agreement with the fundamental

[28] Noyes and Eastman, Carnegie Report No. 19, p. 241.
[29] Harkins, *J. Am. Chem. Soc.* *33*, 1808 (1911).

hypothesis of Arrhenius; namely, that an electrolyte in solution is ionized, and its ionization is a function of the concentration, decreasing with increasing concentration. There exists, therefore, in solutions of electrolytes an equilibrium between the ions and the un-ionized molecules, and this equilibrium must be subject to the usual laws governing equilibria. It is obvious that, according to the law of mass action, the ionization should increase with decreasing concentrations, since there is an increase in the number of molecular species as a result of the reaction. If we assume a simple system, as for example a binary salt MX which forms the ions M^+ and X^-, according to the equation:

$$MX = M^+ + X^-,$$

then, according to the law of mass action, we should have a relation:

$$\frac{C_{M^+} \times C_{X^-}}{C_{MX}} = K, \tag{5}$$

where C_X represents the concentration of the molecular species X. If the solution is sufficiently dilute, so that the laws of dilute solutions may be applied, then K will be a function of the temperature only. On the other hand, it is obvious that a concentration must ultimately be reached where the laws of dilute solutions fail, in which case K becomes a function of the concentration as well as of the temperature.[30]

If γ is the degree of ionization of the salt and if C is its total concentration, then the concentrations of the two ions will be equal to $C\gamma$ and the concentration of the un-ionized fraction will be equal to $C(1 - \gamma)$. If these values are substituted in Equation (5), they lead to the equation:

$$\frac{C\gamma^2}{1 - \gamma} = K. \tag{6}$$

The value of γ may be calculated either from conductance or from osmotic measurements. If the values of γ according to the two methods agree, then obviously the two methods must lead to identical results, so far as the mass-action law is concerned. Since the degree of ionization is given by Equation 2, we may substitute this value of γ in Equation 6 which yields the equation:

$$\frac{C\Lambda^2}{\Lambda_0(\Lambda_0 - \Lambda)} = K. \tag{7}$$

This equation, involving the two constants K and Λ_0, therefore expresses the relation between the concentration and the conductance of a solution

[30] Van der Waals-Kohnstamm, "Lehrbuch der Thermodynamik," part 2, pp. 604, *et seq.*

of a binary electrolyte. In general, to test the applicability of this equation, the value of Λ_0 must first be determined by some method of extrapolation, after which the constancy of the function K may be determined by substituting in the above equation. In Table VII [31] are

TABLE VII.

VALUES OF K FOR ACETIC ACID IN WATER AT 25°.

V	Λ	$K \times 100$
0.989	1.443	0.001405
1.977	2.211	0.001652
3.954	3.221	0.001759
7.908	4.618	0.001814
15.816	6.561	0.001841
31.63	9.260	0.001846
63.26	13.03	0.001846
126.52	18.30	0.001847
253.04	25.60	0.001843
506.1	35.67	0.001841
1012.2	49.50	0.001844
2024.4	68.22	0.001853
∞	387.9	—

given values for the conductance of acetic acid in water at 25° at a series of concentrations. In this table, V denotes the dilution in liters per equivalent, Λ the equivalent conductance and K the ionization constant, calculated according to Equation 7.

It will be seen that at higher concentrations, down to about 0.1 normal, there is a marked change in the value of the function K, but at concentrations below 0.1 normal the function K remains constant, practically within the limits of experimental error.[31a] At the highest dilution in the table the function K shows a slight increase, which is probably due to a discrepancy between the experimental values and the assumed value of Λ_0. In general, the weaker the acid, the greater the range of concentration over which the function K remains constant. In other words, the concentration, at which the function K varies measurably from constancy, increases as the strength of the acid increases. In Table VIII [32] are given values of the equivalent conductance and the ionization constant of trichlorobutyric acid at a series of concentrations. It will be

[31] Kendall, *Med. Veten. Akad. Nobelinstitut* 2, No. 38, p. 1 (1913).
[31a] The decrease in the value of K at higher concentrations is in part, if not largely, due to the increasing viscosity of the solution. Compare Washburn, "Principles of Physical Chemistry," 2nd Ed., p. 340.
[32] Kendall, *loc. cit.*

TABLE VIII.

VALUES OF K FOR TRICHLOROBUTYRIC ACID IN WATER AT 25°.

V	Λ	$K \times 100$
5.90	237.3	18.3
11.80	276.8	17.4
23.59	308.5	15.9
38.63	326.4	14.8
47.18	331.8	14.0
53.98	336.0	13.9
77.26	343.9	12.7
107.96	350.4	11.8
154.5	357.0	11.5
215.9	361.2	10.9
309.0	365.1	10.5
431.8	368.2	10.7
618.0	370.9	(11.6)
∞	376.0	—

observed that the function K decreases throughout as the concentration decreases, but that the decrease is more marked at higher concentrations and that, apparently, at lower concentrations a limiting value is approached. The slight variation in the value of K at the lowest concentrations may be due either to experimental errors or to a discrepancy in the value of Λ_0. In general, we may say that electrolytes, such as acetic acid, fulfill the condition that in the more dilute solutions the function K remains substantially constant. The same holds true in the case of the weak bases.

Obviously, these results afford strong confirmative evidence of the correctness of the fundamental assumption that these electrolytes are ionized in solution according to a reaction equation of the following type:

$$CH_3COOH = CH_3COO^- + H^+.$$

On the other hand, when we proceed to a consideration of typical salts, or what are commonly known as strong electrolytes, we find that K appears throughout to be a function of the concentration, its value decreasing as the concentration decreases.

Below are given the values of the function K at a series of concentrations for solutions of potassium chloride in water at 18°: [33]

[33] The manner in which K varies with the concentration at very low concentrations is uncertain, since small errors in the extrapolated value of Λ_0 cause a large variation in the resulting value of the function K. The values here given are based on the value of Λ_0 derived by the author. *J. Am. Chem. Soc.* *42*, 1 (1920). Compare, also, Weiland, *ibid.*, *40*, 146 (1918).

TABLE IX.

VALUES OF K FOR KCl IN WATER AT 18°.

$C =$	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	1.0
$K =$	.00518	.0147	.0474	.1542	.5052	2.14

It will be observed that in this case the function K decreases enormously with decreasing concentration. Whether the function approaches a finite limit, or whether it approaches a limit zero at low concentrations, cannot be determined with certainty. In general, the stronger the electrolyte, the more does the function K vary with the concentration and the greater is its value at a given concentration. In the case of hydrochloric acid the values of K at a number of concentrations are as follows:

TABLE X.

VALUES OF K FOR HCl IN WATER AT 18°.

$C =$	10^{-3}	10^{-2}	10^{-1}
$K =$	0.189	0.366	1.11

If these values are compared with those for potassium chloride, it will be seen that the value of K is considerably greater for hydrochloric acid than it is for potassium chloride. At 0.1 normal the value of K for hydrochloric acid is approximately twice that for potassium chloride. In the more dilute solutions, however, this ratio appears to increase, since in a 0.001 normal solution the value for hydrochloric acid is approximately four times that of potassium chloride.

In view of the fact that electrolytes of a given type appear to be ionized to practically the same extent in water, it follows that the discrepancies found for different electrolytes of the same type will be of the same order of magnitude.

Chapter III.

The Conductance of Electrolytic Solutions in Various Solvents.

1. *Characteristic Forms of the Conductance-Concentration Curve.* The property of forming solutions which possess the power of conducting the current is one not restricted to water. Nor, indeed, are electrolytes in non-aqueous solvents restricted entirely to those substances which are electrolytes in aqueous solution. As the field of non-aqueous solutions has been extended in recent years, it has become more and more apparent that the property of forming solutions which conduct the current is one which is common to a great many substances. Indeed, it seems not improbable that all liquid non-metallic media yield electrolytic solutions when suitable substances are dissolved in them.

In attempting to account for the properties of electrolytic solutions in water, it is difficult to distinguish between those properties which are characteristic of electrolytic solutions in general and those which are characteristic of aqueous solutions alone. Such a knowledge can be obtained only from a study of the properties of electrolytic solutions in a large variety of solvents, and it appears unlikely that the properties of electrolytic solutions may be successfully accounted for until we possess reliable data as to the properties of non-aqueous solutions. While this field has been greatly extended during the past two decades, it is only in the case of a few solvents that we possess a sufficient mass of facts to enable us to treat the subject with a measurable degree of completeness.

From a constitutional point of view, the alcohols are more nearly related to water than are any other solvents, since they may be looked upon as water in which one of the hydrogen atoms has been substituted by a hydrocarbon group. We should expect the properties of these solvents to diverge progressively from those of water as the size and complexity of the hydrocarbon group increases, and such has indeed been found to be the case. In general, the ionizing power of the alcohols diminishes as the complexity of the carbon group increases. Accordingly, methyl alcohol stands much nearer to water than do any of the other representatives of this class of solvents.

For the purposes of illustration we may consider the conductance of

sodium iodide in ethyl alcohol, the values of which are given in Table XI: [1]

TABLE XI.

CONDUCTANCE OF SODIUM IODIDE IN ETHYL ALCOHOL AT 18°.

V	125	250	500	1000	2000	4000	8000	∞
Λ	28.6	31.3	33.5	35.2	36.5	37.6	38.3	39.4
γ	0.726	0.794	0.850	0.894	0.926	0.954	0.972	1.0

It will be observed that the conductance of solutions in ethyl alcohol increases with decreasing concentration in a manner similar to that of solutions in water. The limiting value of the equivalent conductance, that is the value of Λ_0, for a solution of sodium iodide in ethyl alcohol is in the neighborhood of 39.4. It follows, therefore, that the ionization values of solutions in ethyl alcohol are considerably smaller than those of solutions in water. In Figure 3, the ionization of sodium iodide in ethyl alcohol is shown as a function of concentration. In the same figure, the ionization of sodium chloride in water is likewise shown.

Acetone is another solvent whose solutions resemble those in water in many respects. The conductance of sodium iodide in acetone at 18° at a series of concentrations is given in Table XII: [2]

TABLE XII.

CONDUCTANCE OF SODIUM IODIDE IN ACETONE AT 18°.

V	292.6	1030	4083	8874	18660	39700	64827	∞
Λ	112.8	131.1	147.7	151.0	154.8	155.2	156.0 ?	156.0
γ	0.723	0.841	0.947	0.968	0.992	0.995	—	—

Here, again, it will be observed that the equivalent conductance rises throughout with decreasing concentration. While the conductance values of acetone solutions are greater than those of solutions in ethyl alcohol, the degree of ionization is very nearly the same in the two solvents. In both ethyl alcohol and acetone the ionization is much lower than it is in water.

Another typical solvent is found in liquid sulphur dioxide. The conductance values of solutions of potassium iodide in sulphur dioxide at —33° and at —10° are given in Table XIII: [3]

[1] Dutoit and Rappeport, *Jour. d. Chim.-Phys.* 6, 545 (1908).
[2] Dutoit and Levrier, *Jour. d. Chim.-Phys.* 3, 43 (1905).
[3] Franklin, *J. Phys. Chem.* 15, 675 (1911).

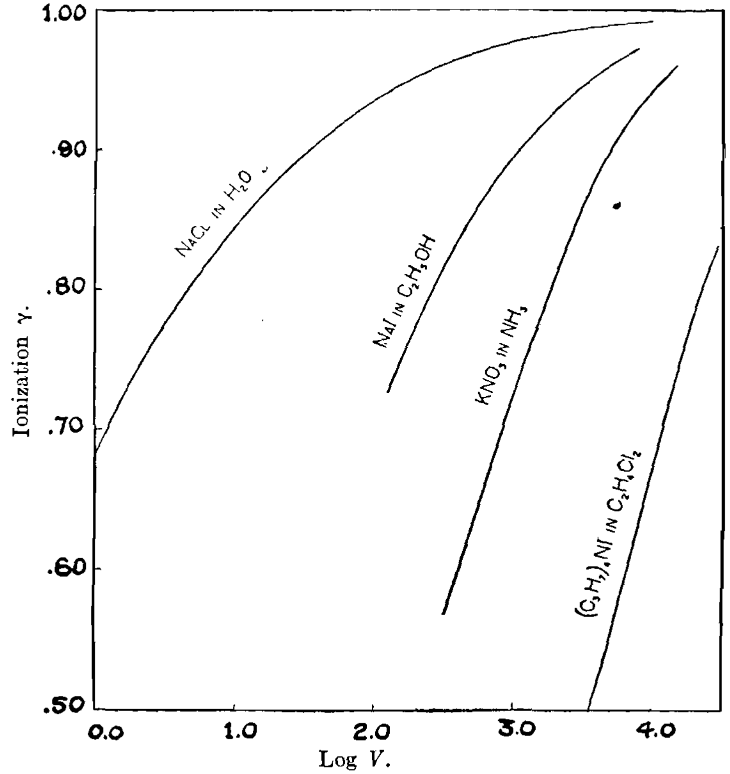

FIG. 3. Ionization of Binary Electrolytes in Different Solvents.

TABLE XIII.

CONDUCTANCE OF KI IN SO_2 AT —33° AND —10°.

V	0.50	1.00	2.0	4.0	8.0	16.0	32.0	64.0
Λ_{-33° ..	27.5	37.7	40.1	40.5	41.0	42.7	47.2	55.1
Λ_{-10° ..	39.7	46.9	46.8	44.8	42.5	43.5	47.8	55.7
V	128.0	256.0	512.0	1000.0	2000.0	4000.0	8000.0	∞
Λ_{-33° ..	65.9	78.8	93.4	108.6	124.2	139.0	153.0	167.5
Λ_{-10° ..	66.5	81.7	99.2	118.8	140.5	162.5	181.8	199.0

Again, we find that as the concentration decreases the equivalent conductance increases and approaches a limiting value in the neighborhood of 167.5 at —33°. The ionization of the solutions of potassium iodide in sulphur dioxide is, however, markedly lower than that of correspond-

ing solutions in acetone and alcohol. At higher concentrations the solutions of potassium iodide exhibit a marked divergence from the aqueous type. While it is true that at —33° the conductance falls throughout as the concentration increases, it will be observed that in the concentration interval between $V = 2$ and $V = 16$ the conductance undergoes only an inappreciable increase, whereas at both higher and lower concentrations the conductance change is quite marked. This behavior of the more concentrated solutions in sulphur dioxide indicates the appearance of a new type of curve. At a slightly higher temperature this irregularity at the higher concentration becomes more pronounced and a maximum and a minimum occurs in the curve, as may be seen from the values given for the conductance of these solutions at —10°. The curve at —10° is a typical example which is met with in the case of a large number of solvents.

Before discussing this case in detail, however, let us examine a type of solution the conductance curve of which has a form radically different from that of aqueous solutions. In Table XIV [4] are given values of the conductance of methyl alcohol in liquid hydrogen bromide at —90°.

TABLE XIV.

CONDUCTANCE OF CH_3OH IN LIQUID HBr AT —90°.

V	0.1250	0.2500	0.500	0.769	1.00	2.00	7.69
Λ	0.600	0.631	0.211	0.0378	0.00925	0.001660	0.000615

It will be observed that in the more dilute solutions the conductance diminishes continuously as the concentration decreases. There is no indication that, at lower concentrations, the conductance approaches a limiting value other than zero. In the more concentrated solutions the conductance increases greatly as the concentration increases, until a maximum is reached, after which the conductance falls off sharply. It is interesting to note also that, in this solvent, methyl alcohol functions as an electrolyte, although in most solvents methyl alcohol exhibits no electrolytic properties. Actually, however, the solutions of methyl alcohol in hydrogen chloride do not differ materially in properties from solutions of typical salts, such as the substituted ammonium salts in this solvent, although the value of the equivalent conductance is larger for typical salts.

Another example of this type of conductance curve is that of solutions of trimethylammonium chloride in liquid bromine. The values of the conductance at 25° are given in Table XV: [5]

[4] Archibald, *J. Am. Chem. Soc.* 29, 665 (1907).
[5] Darby, *J. Am. Chem. Soc.* *40*, 347 (1918).

TABLE XV.

CONDUCTANCE OF TRIMETHYLAMMONIUM CHLORIDE IN BROMINE AT 25°.

C	0.029	0.0595	0.2093	0.3427	0.5334	0.9323	1.236	1.314
Λ	0.0253	0.1038	2.063	5.259	6.469	9.865	11.49	11.00

This case is, if anything, even more extreme than that of methyl alcohol in hydrogen bromide. The increase in the conductance with increasing concentration is extremely marked. At a concentration of 0.029 mols per liter, the equivalent conductance is only 0.0253, whereas at a concentration of 1.236 mols per liter the equivalent conductance is 11.49. It is to be noted that in the neighborhood of normal the equivalent conductance of these solutions in bromine is comparable with that of solutions in ordinary solvents. At slightly lower concentrations, however, this is no longer the case. For a concentration change in the ratio of 43 to 1, the conductance increases in the ratio of approximately 450 to 1.

It is apparent that the relation between the conductance and the concentration, as we observe it in aqueous solutions, is not a property characteristic of electrolytic solutions in general. It represents one extreme of two types of solutions, the other of which is exemplified in solutions in hydrogen bromide and in bromine. Between these two extreme types we have an intermediate type which appears to combine the characteristics of these extreme types. A typical example is furnished by solutions of potassium iodide in methylamine at —33°, values of which are given in Table XVI: [6]

TABLE XVI.

CONDUCTANCE OF KI IN CH_3NH_2 AT —33°.

V	0.6094	1.190	2.320	8.833	33.62	107.4	408.9	1557	5927
Λ	31.12	32.97	28.49	17.40	14.64	17.72	27.79	45.86	74.53

The conductance curve in this case is intermediate in type between that of solutions in water and in bromine. In the more dilute solutions, beginning at a dilution of approximately 33 liters, the conductance increases continuously with decreasing concentration and apparently approaches a limiting value. At a dilution of 33.62 liters, the conductance has a minimum value. At higher concentrations it increases markedly, reaching a maximum in the neighborhood of 1.19 liters, after which it again

These intermediate curves apparently form a continuous series between the two extreme types and, by suitably changing the condition of the solutions, a continuous shift takes place in the curve from one extreme toward the other. For example, as the temperature of a solution is increased, there is a shift from the aqueous type toward the type exemplified by the solutions in hydrogen bromide. This is clearly the case with solutions in sulphur dioxide. As we have already seen, at $-33°$ the conductance of solutions in sulphur dioxide increases continuously with decreasing concentration, although there is a certain concentration interval over which the conductance change is extremely small. At a temperature of $-10°$ this curve exhibits a maximum and a minimum, similar to that just described in the case of solutions in methylamine. At still higher temperatures, the maximum and minimum become more pronounced.

Methylamine may be looked upon as a derivative of ammonia and the relation between methylamine and ammonia solutions may be expected to be similar to that between the alcohols and water. As we shall see presently, ammonia solutions, for the most part, belong to the aqueous type; that is, the conductance increases throughout with decreasing concentration. In the case of methylamine solutions, as we have seen, the curve exhibits a pronounced maximum and minimum. Solutions in ethylamine are still further removed toward the bromine type, as is apparent from the values given for the conductance of silver nitrate in ethylamine in Table XVII: [7]

TABLE XVII.

CONDUCTANCE OF $AgNO_3$ IN $C_2H_5NH_2$ AT $-33°$.

V	0.9928	1.981	3.953	15.73	62.65	125.0
Λ	5.67	5.820	4.320	1.677	1.038	1.041

In this case the conductance decreases with decreasing concentration, but it is evident that at the lower concentrations the conductance does not approach the value zero as a limit. In fact, it is apparent that, at dilutions slightly greater than 125 liters per mol, the conductance curve will again rise. Indeed, solutions of certain other salts in ethylamine exhibit a distinct minimum in the neighborhood of 0.01 normal. The conductance curve of solutions in amylamine resembles that of solutions in bromine very closely, the conductance decreasing throughout

It is evident that, in order to account for the phenomena of electrolytic solutions, it is necessary to take into consideration the fact that the form of the conductance curve as observed in water is not a general type, but is only one extreme of several types. Any comprehensive theory of electrolytic solutions must obviously account for both types.

The only non-aqueous solvent with regard to whose solutions we have anything like complete information at the present time is liquid ammonia. This solvent yields electrolytic solutions with an extremely large variety of substances and we shall have frequent occasion to refer to these solutions below. At this point it will be sufficient to give an example of the conductance curve for a typical salt dissolved in liquid ammonia. In Table XVIII [8] are given values of the conductance of solutions of potassium nitrate in liquid ammonia at its boiling point, approximately —33°, at a series of dilutions. It is evident that these solutions belong to the aqueous type, the conductance increasing throughout with decreasing concentration and approaching a limiting value at very low concentrations. The limiting value for potassium nitrate is 339.[9]

TABLE XVIII.

CONDUCTANCE OF KNO_3 IN NH_3 AT —33°.

V	324	1001	2514	6162	23060	69820	∞
Λ	192.7	245.0	282.7	309.9	330.1	338.6	339.
γ	0.567	0.720	0.831	0.912	0.972	0.995	

Solutions of typical salts in liquid ammonia exhibit a somewhat higher conductance than do the corresponding salts in water, but it is evident that the ionization of these salts in liquid ammonia solutions is considerably lower than in water, as may be seen from Figure 3. Ammonia apparently approaches ordinary alcohol and acetone in its ionizing power. In the case of certain solutions in liquid ammonia, an intermediate type of conductance curve is found. This is the case, for example, with potassium amide whose curve exhibits a minimum.[10]

A similar, but in some respects a slightly different, case is found in certain of the cyanides, of which mercuric cyanide and silver cyanide may serve as examples. The conductance values for solutions of mercuric cyanide in ammonia are given in Table XIX.[11]

[8] Franklin and Kraus, *Am. Chem. J.* *23*, 277 (1900).
[9] Kraus and Bray, *J. Am. Chem. Soc.* *35*, 1337 (1913).
[10] Franklin, *Ztschr. f. phys. Chem.* *69*, 290 (1909).
[11] Franklin and Kraus, *loc. cit.*

TABLE XIX.

CONDUCTANCE OF $Hg(CN)_2$ IN NH_3 AT —33°.

V	1.16	3.37	5.71	21.8	33.0	55.6
Λ	2.48	1.86	1.79	1.63	1.64	1.75

The solutions of this salt exhibit a conductance curve with a very flat minimum, the curve thus being similar to that of potassium iodide in methylamine. Silver cyanide likewise exhibits a curve with a minimum. The values are given in Table XX.[12]

TABLE XX.

CONDUCTANCE OF AgCN IN NH_3 AT —33°.

V	4.48	9.02	17.85	35.25	69.69	137.7	272.8	538.0	1063.0
Λ	15.58	15.39	14.28	13.45	12.83	12.41	12.12	12.00	12.00

It is evident from these values that the conductance curve for silver cyanide has a very flat minimum in the neighborhood of 10^{-3} normal. What is more striking, however, is the fact that the conductance changes so little with the concentration. The entire change between 10^{-3} normal and 0.5 normal is only from 12.00 to 15.5 or about 30 per cent.

We see that solutions in non-aqueous solvents exhibit a great variety of properties many of which diverge largely from those of aqueous solutions. A great variety of liquids are capable of forming electrolytic solutions with various substances and many substances which do not form electrolytic solutions when dissolved in water form such solutions in other solvents.

2. *Applicability of the Mass-Action Law to Non-Aqueous Solutions.* From a study of aqueous solutions of electrolytes, the conclusion was reached that the conductance is due to the motion of charged carriers through these solutions and that these charged carriers are in equilibrium with the neutral molecules of the electrolyte. In other words, the electrolyte is dissociated, or ionized, to use the accepted term for this process, and the degree of ionization may be measured by means of the ratio of the equivalent conductance of the solution to the limiting value which the equivalent conductance approaches as the concentration diminishes indefinitely. If this hypothesis is correct, then, as we have seen, the mass-action law should apply, and, if the laws of dilute solutions may be assumed to hold, Equation 7 expresses the relation between the conductance and the concentration of an electrolytic solution. It was found

[12] Franklin and Kraus, *loc. cit.*

that this relation is fulfilled in the case of aqueous solutions of weak acids and bases, but is not fulfilled in the case of solutions of electrolytes which are more largely ionized.

It is at once apparent that non-aqueous solutions furnish exceptions to the simple mass-action law, since we have here cases in which the conductance increases with increasing concentration, which result is not in accord with Equation 7. To solve the problem resulting from this discrepancy, three methods of attack at once present themselves. In the first place, the ionization may not be correctly measured by the ratio Λ/Λ_0. Then, again, we may assume that the reaction equation on which the calculations are based is not correct. Finally, we may assume that the equilibrium is of the type as assumed, but the conditions assumed in deriving the mass-action law are not fulfilled in the solutions in question; in other words, the solutions may not be considered as dilute. It is of course impossible to state on *a priori* grounds the concentration at which the deviations from the laws of dilute solutions will become appreciable. The only method that we have of attacking this problem at present is to carry out measurements at different concentrations and examine the change in the mass-action function as the concentration decreases. If the fundamental assumption underlying the hypothesis of Arrhenius is correct, then the mass-action function should approach a definite limiting value as the concentration decreases.

Let us examine, therefore, the conductance curves of the more dilute non-aqueous solutions in order to determine whether the mass-action function approaches a definite limiting value. It is obvious that, in order to calculate the degree of ionization, the value of Λ_0 must be known and this value can be obtained only by extrapolation. If the mass-action equation in its simple form actually holds, then it is possible to determine the value of Λ_0 by a very simple graphical extrapolation. Equation 7 may be written in the form:

$$C\Lambda = \frac{K\Lambda_0^2}{\Lambda} - K\Lambda_0. \tag{8}$$

It is obvious that, if this equation holds, the reciprocal of the equivalent conductance, Λ, is a linear function of $C\Lambda$, which is equal to the specific conductance multiplied by 10^3. In other words, if the mass-action law is obeyed, the reciprocal of the equivalent conductance and the specific conductance are connected by means of a linear equation. If, therefore, the experimental values of $C\Lambda$ and of $1/\Lambda$ are plotted in a system of rectangular co-ordinates, the points will lie on a straight line if the mass-action law holds. This straight line extrapolated to the axis of $1/\Lambda$

yields the value of Λ_0 while, obviously, the value of K results from the slope of the curve.

Leaving aside for the moment the exact values of Λ_0, we may roughly compare the variation of the function K for solutions in different solvents. In Table XXI [13] are given the values of this function for potassium nitrate dissolved in ammonia and in water at corresponding degrees of ionization.

TABLE XXI.

VALUES OF K FOR SOLUTIONS OF KNO_3 IN NH_3 AND H_2O.

γ	$K_{NH_3} \times 10^{-2}$	K_{H_2O}
57.00	0.2277	1.279
70.00	0.197	0.9528
85.59	0.167	0.3389
91.66	0.1635	0.2332
94.30	0.1699	0.1710

It is at once apparent that the variation of the function K in dilute ammonia solutions is much less than it is in aqueous solutions. Indeed, between the ionization values of 70% and 94% the value of the conductance function for potassium nitrate in ammonia changes only by a few per cent, whereas, in aqueous solutions, this function increases approximately five times. Apparently, therefore, dilute solutions in ammonia approach the mass-action law much more nearly than do solutions of the same substances in water.

A circumstance which greatly facilitates the study of the applicability of the mass-action law to dilute solutions in non-aqueous solvents is the relatively low ionization of the solutions in these solvents. In the case of the strong electrolytes in water, a comparison of the experimental results with the mass-action law is rendered difficult by the high ionization of these salts. Since the expression $1-\gamma$, the value of the un-ionized fraction, appears in the denominator of the mass-action expression, and since γ is very nearly unity, it follows that the equivalent conductance must be determined with a high degree of precision in order to determine the applicability of the mass-action function. It is only in the case of potassium chloride that sufficiently precise data are at hand to make a study of this kind possible in aqueous solutions, and even in this case the results of such a comparison remain uncertain.

Only a small portion of the data relating to the conductance of non-aqueous solutions has sufficient precision to make a comparison with the consequences of the mass-action law possible. It is only in the case of

[13] Franklin and Kraus, *Am. Chem. J.* 23, 299 (1900).

solutions in liquid ammonia that we have such data relating to a large number of electrolytes. Kraus and Bray [14] have examined the conductance of ammonia solutions from this point of view. In Figures 4 and 5 are plotted values of the reciprocal of the equivalent conductance as

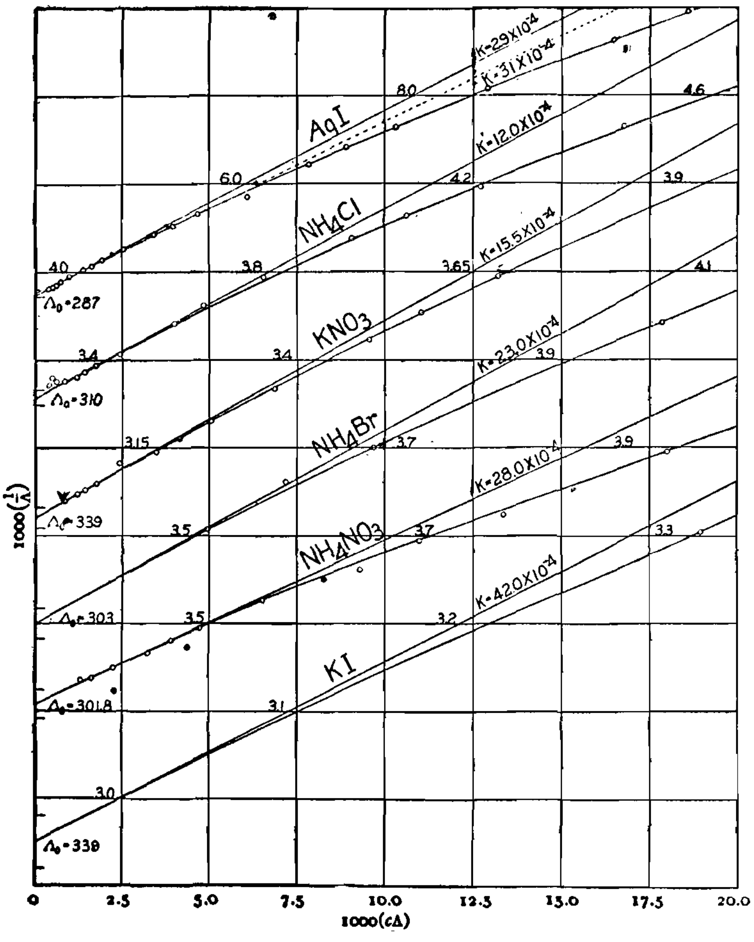

FIG. 4. Showing Approach of Dilute Solutions in Liquid NH_3 to the Mass-Action Law.

ordinates against values of the specific conductance as abscissas. In Figure 4 the symbol of the electrolyte is shown in the figure, while in Figure 5 the curves in order from 1 to 7 are for: 1, thiobenzamide; 2, orthomethoxybenzenesulphonamide; 3, paramethoxybenzenesulphona-

[14] Kraus and Bray, *J. Am. Chem. Soc.* 35, 1315 (1913).

mide; 4, metamethoxybenzenesulphonamide; 5, nitromethane; 6, sodium-nitromethane; and 7, orthonitrophenol. Examining the figure for the typical salts, it will be observed that in the case of silver iodide, ammonium chloride, potassium nitrate, and ammonium nitrate the curves

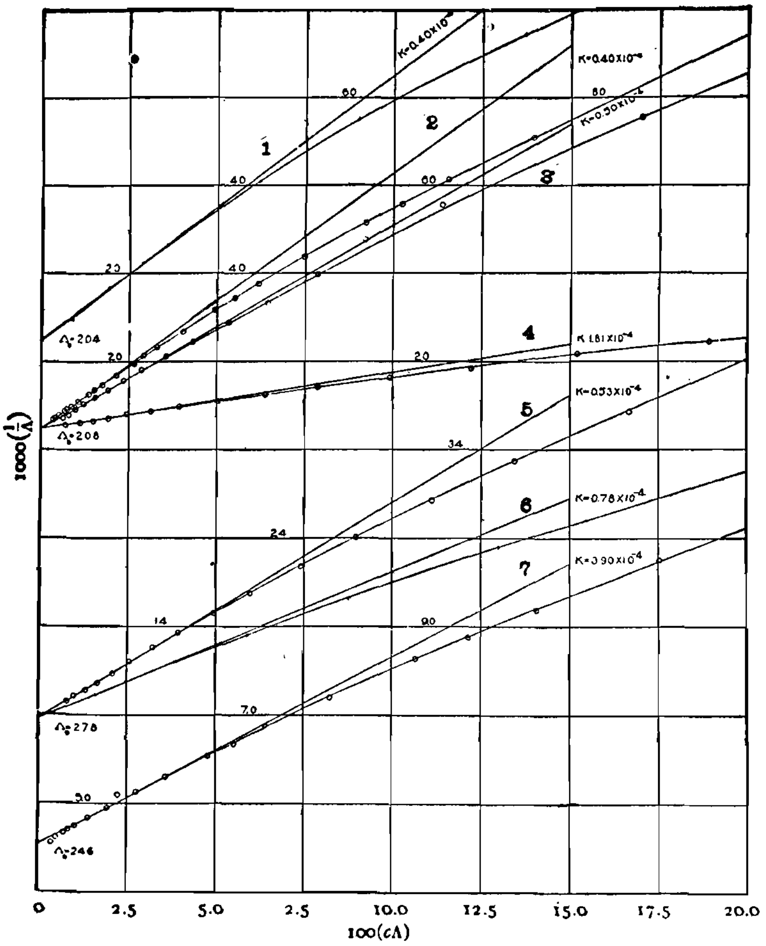

FIG. 5. Showing Approach of Dilute Solutions of Organic Electrolytes in NH_3 to the Mass-Action Law.

in dilute solution approach a straight line. In the case of ammonium bromide and potassium iodide the number of points is not sufficient to actually determine the form of the curve in dilute solutions. In the case of other salts, the figures of which are not shown here, similar results were obtained; that is, in those cases where sufficient data are available at low concentrations, the points approximate a straight line and this

is the more true the more consistent the data are among themselves. In the case of the seven electrolytes in Figure 5, the correspondence with the mass-action law is much more certain. One reason for the better agreement in the case of these electrolytes is their lower ionization, as a result of which errors in the value of the equivalent conductance produce a smaller variation in the mass-action constant. Moreover, in these cases the mass-action law appears to apply to greater total salt concentrations. In view of the fact that the original experimental results are independent of any considerations as to the applicability of the mass-action law, the conclusion appears justified that in the case of solutions in liquid ammonia the mass-action function approaches a limiting value at low concentrations.

The total salt concentration at which the deviations from the simple mass-action law become appreciable is the lower, the greater the ionization of the electrolyte. In this respect solutions in ammonia resemble solutions of the acids and bases in water. The lower the ionization of an acid or a base in water, the higher the concentration up to which the mass-action law appears to hold. From an examination of their results, Kraus and Bray drew the conclusion, however, that the deviations from the mass-action law become appreciable for different electrolytes in ammonia solution at about the same ion concentration. They found that the mass-action function for a number of electrolytes was increased over the limiting value by 5% at ion concentrations lying in the neighborhood of 1×10^{-4} N. It is, however, apparent that in certain cases the ion concentration is considerably greater and in other cases considerably lower than this value. So, for example, in the case of potassium amide this concentration is 2.76×10^{-4}, while in that of trinitraniline it is 0.22×10^{-4}.

We may now consider the values of the mass-action constant for different electrolytes in ammonia solution. The values for the inorganic electrolytes are given in Table XXII[15] (see opposite page).

It is apparent, in the first place, that the values of the mass-action constant for the different inorganic electrolytes differ considerably. The extreme values lie between 0.056×10^{-4} for sodium amide and 42×10^{-4} for potassium iodide. The greater number of the salts, however, have ionization constants lying between 21×10^{-4} and 28×10^{-4}. This variation of the ionization constants for different inorganic electrolytes in ammonia is in striking contrast with the nearly identical ionization of the same electrolytes in water. It should be borne in mind, however, that in aqueous solution the degree of ionization is so high, in any case, that dif-

[15] Kraus and Bray, *loc. cit.*

TABLE XXII.

VALUES OF K AND Λ_0 FOR DIFFERENT ELECTROLYTES IN NH_3 AT —33°.

Salt	10^4K	Λ_0
$NaNH_2$	0.056	263
KNH_2	1.20	301
AgI	2.90	287
NH_4Cl	12.0	310
NaCl	14.5	309
KNO_3	15.5	339
KBr	21.0	340
$TlNO_3$	21.0	323
$NaBrO_3$	23.0	378
$NaNO_3$	23.0	301
NH_4Br	23.0	303
$LiNO_3$	26.0	283
NaBr	27.0	302
NaI	28.0	301
$AgNO_3$	28.0	287
NH_4NO_3	28.0	302
KI	42.0	339

ferences in the ionization values of the different electrolytes are necessarily very small. Nevertheless, we must conclude that the ionization values of typical salts in water are much more nearly the same in that solvent than they are in ammonia or in any other solvent for which reliable data are available. The order of the ionization constants does not appear to bear any relation to the constitution of the electrolytes. So ammonium chloride has an ionization constant of 12×10^{-4} and ammonium nitrate of 28×10^{-4}, while silver iodide has an ionization constant of 2.9×10^{-4} and silver nitrate 28×10^{-4}. Sodium nitrate has a greater ionization constant than potassium nitrate, while sodium iodide has a smaller ionization constant than potassium iodide.

The constants for sodium and potassium amides are of interest owing to the fact that these substances are bases in liquid ammonia solution. Apparently these substances are relatively weak bases when compared with the typical salts in ammonia or when compared with corresponding bases in water. Indeed, it is apparent that all electrolytes in ammonia solution have comparatively small ionization constants. For example, the ionization constant of acetic acid in water is 0.182×10^{-4}. The ionization constant of this acid, therefore, is approximately three times that of sodium amide and 1/7 that of potassium amide.

The ionization constants for a number of organic electrolytes in liquid

ammonia are given in Table XXIII.[16] Here, again, we find a large variation in the value of the ionization constant for different electrolytes.

TABLE XXIII.

VALUES OF K AND OF Λ_0 FOR ORGANIC ELECTROLYTES IN NH_3 AT —33°.

Salt	$10^4 K$	Λ_0
Cyanacetamide	0.045	260
Thiobenzamide	0.40	204
Orthomethoxybenzenesulphonamide	0.40	208
Paramethoxybenzenesulphonamide	0.50	208
Nitromethane	0.53	278
Sodiumnitromethane	0.78	278
Benzenesulphonamide	1.39	208
Metamethoxybenzenesulphonamide	1.81	208
Orthonitrophenol	3.90	246
Methylnitramine	8.4	256
Phthalimide	8.7	248
Benzoicsulphinide	12.0	206
Metanitrobenzenesulphonamide	12.5	231
Potassiummetanitrobenzenesulphonate	15.0	275
Nitrourethaneammonium	21.6	262
Trinitrobenzene	30.0	234
Trinitraniline	30.0	234

The strongest of these, trinitraniline and trinitrobenzene, have ionization constants as great, or greater, than those of typical salts in ammonia. On the other hand, cyanacetamide has an ionization constant of only 0.045×10^{-4}. Cyanacetamide, therefore, is a weaker acid in ammonia solution than acetic acid is in water, and of course a much weaker acid than cyanacetic acid in water. In other respects, as regards the relation of the ionization constants of these electrolytes to their constitution, we find relations similar to those in aqueous solutions. The introduction of strongly electronegative groups into the negative constituent increases the value of the ionization constant. It will be observed that many of the organic substances which act as electrolytes in ammonia solution are not electrolytes in water. This is true of nearly all the acid amides and of such compounds as trinitrobenzene. The positive ion, in the case of the acid amides, as indeed in the case of all the acids in ammonia solution, is presumably the ammonium ion.[17]

Having seen that the mass-action law applies to dilute solutions of practically all electrolytes in ammonia, we may inquire whether the same

[16] Kraus and Bray, *loc. cit.*
[17] *Ibid., loc. cit., p.* 1357.

is true of solutions in other non-aqueous solvents. In Table XXIV[18] are given values of the mass-action constants for sodium iodide in a number of different solvents. In Figure 6 are plotted values of the reciprocal conductance against those of the specific conductance for these solutions.

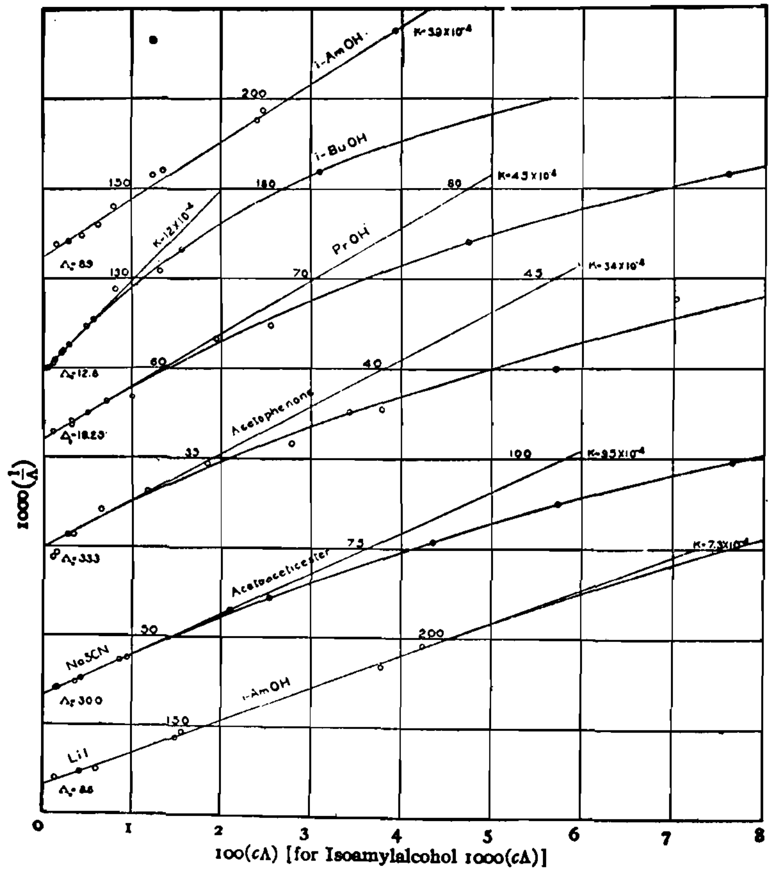

FIG. 6. Showing how Solutions of Binary Electrolytes in Different Solvents Approach the Mass-Action Relation at Low Concentrations.

An examination of the figure shows that in all cases the conductance curves approach a linear relation in the more dilute solutions. We may conclude, therefore, that in the case of non-aqueous solvents, in general, the mass-action law is approached as a limiting form at low concentrations.

[18] Kraus and Bray, *loc. cit.*

TABLE XXIV.

VALUES OF K AND OF Λ_0 FOR ELECTROLYTES IN DIFFERENT SOLVENTS.

Solvent	Solute	Temp. °C.	$K \times 10^4$	Λ_0
Benzonitrile	NaI	25°	55.0	49.0
Epichlorhydrin	$(C_2H_5)_4NI$	25°	48.5	62.1
Propylalcohol	NaI	18°	45.0	20.6
Acetone	NaI	18°	30.0	167.0
Acetophenone	NaI	25°	34.0	35.6
Methylethylketone	NaI	25°	23.0	139.0
Pyridine	NaI	18°	13.0	61.0
Isobutylalcohol	NaI	25°	12.0	13.7
Acetoaceticester	NaSCN	18°	9.5	32.1
Isoamylalcohol	NaI	25°	3.9	9.2
Ethylenechloride	$(C_3H_7)_4NI$	25°	1.45	66.7

The mass-action constant varies with the nature of the solvent. The greatest value is that for benzonitrile, which is 55×10^{-4}, and the smallest that for ethylenechloride, which is 1.45×10^{-4}. The change in the value of the ionization constant among the alcohols is of particular interest in view of their relation to water. The constant for solutions in propyl alcohol is 45×10^{-4}, in isobutylalcohol 12×10^{-4}, and in isoamylalcohol 3.9×10^{-4}. It is evident that, as the substituting hydrocarbon group becomes more complex, the ionization constant decreases. These results also have a bearing on the probable behavior of aqueous solutions. The properties of solutions in the lower alcohols differ only inconsiderably from those of aqueous solutions. It seems probable, therefore, that in going from water through the lower alcohols to the higher alcohols the change in the phenomenon underlying the ionization process undergoes an alteration in degree rather than in kind. It might be concluded, therefore, that in aqueous solutions, also, the mass-action law is approached as a limiting form. This question, however, will be discussed at somewhat greater length in a succeeding chapter.

A considerable number of data are available on the conductance of dilute solutions in acetone. In the following table are given values of the mass-action constant and the limiting values of the equivalent conductance for a series of electrolytes in this solvent.

TABLE XXV.

VALUES OF K AND OF Λ_0 FOR DIFFERENT ELECTROLYTES IN ACETONE AT 18°.

Solute	$10^4 K$	Λ_0
KI	51.0	156
NaI	39.0	156
LiI	31.0	154

TABLE XXV.—*Continued.*

Solute	$10^4 K$	Λ_0
NH_4I	15.0	159
KSCN	31.0	169
LiSCN	18.0	167
NH_4SCN	8.3	172
KBr	16.0	156
NaBr	13.0	156
LiBr	5.7	154
NH_4Br	2.3	159
$LiNO_3$	2.6	125
$AgNO_3$	0.28	100
LiCl	0.94	154

From an examination of this table it is obvious that the ionization constants of typical salts in acetone vary within very wide limits. So, the ionization constant for silver nitrate is 0.28×10^{-4}, whereas that for potassium iodide is 51.0×10^{-4}. More remarkable still is the regularity in the variation of the constants as a function of the constitution of the electrolyte. The ionization constants of the iodides diminish in the order potassium, sodium, lithium, ammonium. The same order holds in the case of all other salts, namely the sulfocyanates, bromides, and nitrates. On the other hand, the ionization constants of salts with a common positive ion vary in the order: iodides, sulfocyanates, bromides, nitrates, chlorides. This order holds true in every case. It appears, therefore, that the ionization constant K is an additive function of the constituent ions of the electrolytes. This is the only solvent for which such a relation appears to hold true. What the significance of this may be is at present uncertain. It is important, however, to observe that the ionization of different typical salts in acetone varies within extremely wide limits. The similarity in the behavior of strong electrolytes in aqueous solutions, as regards their ionization, is therefore not to be considered as a property which may be ascribed primarily to the electrolytes themselves, but rather one in which the solvent itself appears as the chief factor.

3. *Comparison of the Ion Conductances in Different Solvents.* If the values of Λ_0 are known and if the transference numbers of the electrolytes are known, then the values of the ion conductances may be determined. However, before proceeding to a comparison of the values of the ion conductances in different solvents, it will be well to point out that the value of Λ_0 is dependent upon the form of the extrapolation function which must be assumed. Only in the case of solutions which

approach the mass-action law as a limiting form may we be reasonably certain that the extrapolated value of Λ_0 is correct. In other cases, therefore, the limiting conductance values are more or less arbitrary. In a subsequent chapter this question will be discussed somewhat more at length. For the present we shall assume that the Λ_0 values obtained by the ordinary methods of extrapolation are approximately correct.

The values of the equivalent conductances of the different electrolytes in ammonia and water have been given in Tables III, XXII and XXIII. In comparing the conductances in the two solvents, however, it is preferable to compare the conductance of the individual ions, rather than that of the sum of the ions of any given electrolyte. Before proceeding further, therefore, we shall resolve these values of the conductance for the various electrolytes into two parts, namely the conductance of the positive and of the negative ion respectively. In order that this may be done, it is necessary that the transference number of at least one electrolyte shall be known. In the case of ammonia solutions the transference numbers of a considerable number of electrolytes have been determined by Franklin and Cady.[19] With the aid of their data, the following values of the equivalent conductance of the typical inorganic ions have been calculated.[20] For the sake of comparison, the ion conductances of the same ions in water at 18° are given as well as the ratio of the ion conductances in ammonia and in water.

TABLE XXVI.

ION CONDUCTANCES IN AMMONIA AND IN WATER.

	Ion	In NH_3	In H_2O	$\Lambda_{NH_3}/\Lambda_{H_2O}$
Positive	Li^+	112	33.3	3.36
	Ag^+	116	54.0	2.15
	Na^+	130	43.4	3.00
	NH_4^+	131	64.7	2.03
	Tl^+	152	65.9	2.31
	K^+	168	64.5	2.61
Negative	BrO_3^-	148	47.6	3.11
	NO_3^-	171	61.8	2.77
	I^-	171	66.6	2.57
	Br^-	172	67.7	2.54
	Cl^-	179	65.5	2.73
	NH_2^-	133		

[19] Franklin and Cady, *J. Am. Chem. Soc.* *26*, 499 (1904).
[20] Kraus and Bray, *loc. cit.*

It will be observed that the ion conductances in ammonia and in water do not stand in a fixed ratio. For example, for the silver ion, the ion conductance in ammonia is 2.15 times that in water, whereas for the lithium ion the conductance in ammonia is 3.36 times that in water. Similarly, the conductance of the bromide ion in ammonia is 2.54 times that in water, while the conductance of the bromate ion is 3.11 times that in water. We may naturally inquire as to what are the factors upon which depends the conductance of different ions in different solvents.

If the current is carried through a solution by the translation of charged particles of molecular dimensions, then we should expect the speed of these particles to be a function of the viscosity of the medium through which they move. It might be assumed, for example, that the conductance is proportional to the reciprocal of the viscosity, or to the fluidity of the solvent. The viscosity of water at 18° is 10.63×10^{-3} and that of ammonia is 2.558×10^{-3} at its boiling point. Consequently the fluidity of ammonia is 4.15 times as great as that of water. If the conductance of the ions were directly proportional to the fluidity of the solvent, then the conductance of all ions in ammonia should be 4.15 times as great as that of the same ions in water. We see, however, that while the conductance of the various ions in ammonia is markedly greater than that in water, nevertheless the ratio of the ion conductances in the two solvents is in all cases smaller than this value. Furthermore, the effect is one specific with respect to the individual ions. For example, for the sodium ion, the value is 3.0, while for the lithium ion it is 3.36. It is noticeable that the ratio for the ions increases in the order: ammonium, potassium, sodium, lithium. In other words, in ammonia the lithium ion possesses a relatively much higher conductance with respect to water than does the ammonium ion.

The same general relations hold in the case of the negative ions. The conductance of the bromate ion in ammonia is 3.11 times that in water, whereas that of the bromide ion is only 2.54 times that in water. On the whole, the ion conductances in ammonia vary less than they do in water. The extreme variation in the case of ammonia solutions is from 112, for the lithium ion, to 168, for the potassium ion, or a ratio of 1.5, whereas in the case of aqueous solutions the extreme variation is from 33.3, for the lithium ion, to 65.9, for the thallous ion, or a ratio of 1.98. For the negative ions in ammonia solution the extreme ratio is 1.21, whereas for aqueous solutions it is 1.37. In general, however, the order of ionic conductances in the two solvents is the same. With a few exceptions, ions which move very slowly in water also move very slowly in ammonia.

It is evident that the conductance of an ion is a function of the constitution of the solvent as well as of that of the ion itself. In this connection it should be observed that a given electrolyte dissolved in two different solvents does not necessarily yield the same ions. In other words, complexes may be formed between the ions and the solvent properties of which will depend upon the nature of the solvent. It is well known that certain ions tend to form complexes with certain solvents. For example, the silver ion forms a complex with ammonia even in aqueous solutions. It may be assumed, therefore, that the silver ion has a great tendency to form complexes with ammonia. The cause for the relatively low value of the conductance of the silver ion in ammonia may be ascribed to the formation of a relatively large complex silver-ammonia ion in ammonia solution. Similarly, those ions whose salts show a marked tendency to form complexes with water, which, for example, give stable crystalline hydrates, show a relatively higher speed in ammonia than in water. Thus, the speed of the lithium ion in ammonia is relatively much greater with respect to its speed in water than is that of the potassium ion. We may therefore conclude that the lithium ion is relatively less complex in ammonia than it is in water.

Chapter IV.

Form of the Conductance Function.

1. *The Functional Relation between Conductance and Concentration.* If an equilibrium exists between the ions and the un-ionized molecules in a solution, then the relation between the conductance and the concentration is expressed by Equation 7, which follows from the mass-action law. We have seen that this equation is fulfilled in solutions of weak electrolytes in water and that it is approached as a limiting form in solutions of strong electrolytes in non-aqueous solvents. This equation is the only one so far suggested to account for the relation between the conductance and the concentration which has a substantial theoretical foundation for its support. At higher concentrations, in the case of the stronger electrolytes, both in water and in non-aqueous solvents, the simple form of the mass-action law no longer holds. Except at very high concentrations, where viscosity effects become pronounced, the conductance in all cases varies in such a way that the value of the mass-action function increases with increasing concentration. If the reciprocal of the equivalent conductance is plotted against the specific conductance, then, in the case of strong electrolytes, it is found that the experimental curve is concave toward the axis of specific conductances.

We have seen that in different solvents the conductance curve, as a function of the concentration, varies greatly in form, and the conclusion might be drawn that the process involved in these solutions is entirely different in character. Since the form of the conductance function in the case of the concentrated solutions is thus far not determinable from theoretical considerations, various attempts have been made to determine empirical functions which should express the conductance in terms of the concentration. In the case of aqueous solutions the equation of Storch [1] appears to apply over a considerable concentration range. This equation may be written in the form:

$$K' = \frac{(C\gamma)^2}{C(1-\gamma)} = D(C\gamma)^m, \tag{9}$$

where D and m are constants. This equation applies remarkably well in the case of aqueous solutions, even up to high concentrations. It will

[1] Storch, *Ztschr. f. phys. Chem.* **19**, 13 (1896).

be observed that in this equation the mass-action function K' is expressed as a function of the ion concentration raised to the m'th power. The equation may be tested very simply by graphical methods. It may be written in the form:

$$(10) \qquad (2-m)\log(C\gamma) - \log[C(1-\gamma)] = \log D.$$

If, therefore, we plot the logarithms of $C(1-\gamma)$ against the logarithms of the ion concentrations $C\gamma$ or the specific conductances, the experimental points should lie on a straight line, provided the equation holds. This method of treatment was first proposed by Bancroft[2] and has proved extremely useful in determining the behavior of very concentrated solutions. In Figure 7 are shown the curves for potassium chloride and potassium nitrate in water at 18°. It will be observed that the points lie very nearly on a straight line.

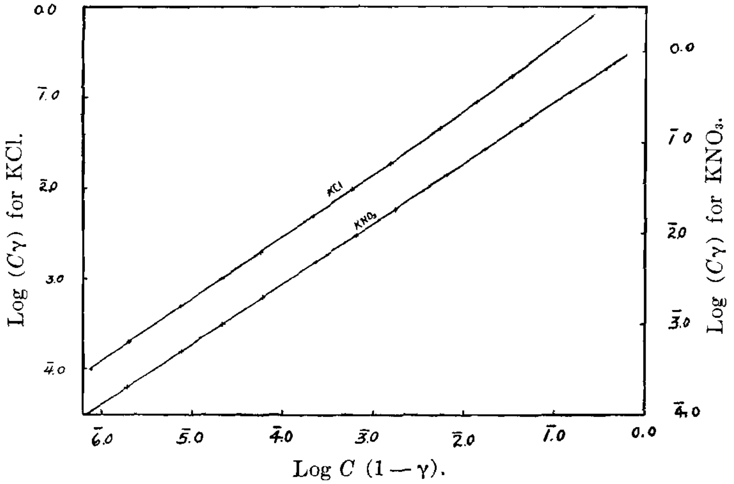

FIG. 7. Plot of Storch Equation for Aqueous Solutions of Binary Electrolytes.

It is evident, however, that an equation of this type cannot apply generally, since it does not approach the mass-action expression as a limiting form. As we have seen, dilute solutions in non-aqueous solvents approach the mass-action function at low concentrations. It has therefore been proposed[3] to express the relation between the conductance and the concentration by means of the equation:

$$(11) \qquad K' = \frac{(C\gamma)^2}{C(1-\gamma)} = D(C\gamma)^m + K.$$

[2] Bancroft, *Ztschr. f. phys. Chem.* *31*, 188 (1899).
[3] Kraus, *Proc. Am. Chem. Soc.* *1909*, p. 15; Bray, *Science* *35*, 433 (1912); *Trans. Am. Electro-Ch. Soc.* *21*, 143 (1912); MacDougall, *J. Am. Chem. Soc.* *34*, 855 (1912); Kraus and Bray, *J. Am. Chem. Soc.* *35*, 1315 (1913). Somewhat similar four-constant equations

In this equation γ is written for the ratio $\frac{\Lambda}{\Lambda_0}$ for the sake of brevity. An inspection of this equation shows that at low concentrations the first term of the right-hand member, involving the ion concentration $C\gamma$, will diminish as the concentration decreases, and will ultimately become negligible in comparison with the constant K. On the other hand, at higher concentrations, the constant K will become negligible in comparison with the term involving the ion concentration. In other words, at high concentrations this equation approaches the Storch Equation 9 as a limiting form.

Obviously, this equation involves the four constants Λ_0, K, D and m. These constants may in most cases be determined readily by graphical means. If conductance data are available at very low concentrations, the second term of the right-hand member may be neglected, in which case the reciprocal of the equivalent conductance becomes a linear function of the ion concentration; that is, the equation degenerates into the form of Equation 7. The value of Λ_0 and of K may therefore be determined with a considerable degree of precision from this plot. Having determined these two constants, the values of m and D may be determined from data at higher concentrations. At very high concentrations K may be neglected and from a plot of Equation 10, which is linear if the equation holds, the values of m and D may be determined. In case the constant K is not negligible at higher concentrations, it is necessary to take this into account. This may be done by means of a second approximation. It is seen from Equation 11 that the mass-action function $K' = \frac{C\gamma^2}{1 - \gamma}$ is a linear function of the ion concentration raised to the m'th power. If the value of m in the more concentrated solutions, as determined by the first approximation, is correct, then the values of K and D may be corrected by means of a plot of K' against $(C\gamma)^m$. The value of K is then determined by extrapolating to the concentration zero and the value of D is determined from the slope of the line. The values of the constants having been determined, it is possible to calculate the conductance of a given electrolyte at any desired concentration and to compare the calculated with the experimental values.

In Figure 8 is shown a plot of the reciprocal of the equivalent conductance against the specific conductance or ion concentration for solutions of potassium amide in liquid ammonia.[4] This plot yields for Λ_0

have been proposed by Bates (*J. Am. Chem. Soc.* 37, 1431 (1915)) and by de Szyszkowski (*Medd. K. Vet. Akad's Nobelinstitut*, Vol. 3, Nos. 2 and 11 (1914)). While these latter equations represent the course of the conductance curve fairly well in the case of aqueous solutions, they are not generally applicable to non-aqueous solutions.

[4] Franklin, *Ztschr. f. phys. Chem.* 69, 290 (1909).

the value 301 and for K the value 1.26×10^{-4}.[5] That is, the straight line drawn corresponding to this slope passes through the points in the more dilute solutions.

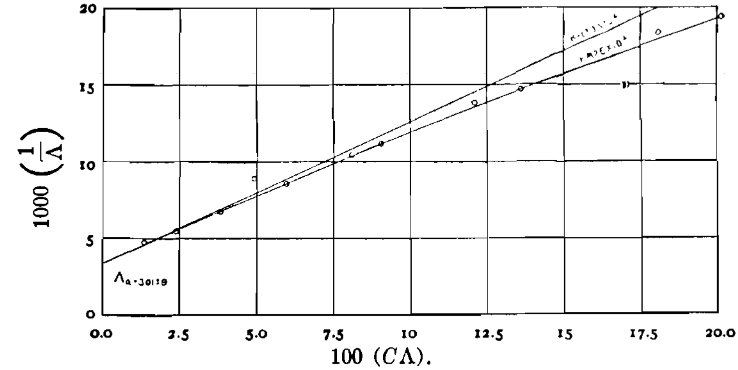

FIG. 8. $\Lambda_0 - K$ Plot for KNH_2 in NH_3.

Having determined the preliminary values of K and of Λ_0, we may plot the values of the logarithm of $K' - K$ against the logarithm of $C\gamma$. The plot for this function is shown in Figure 9, where it will be observed

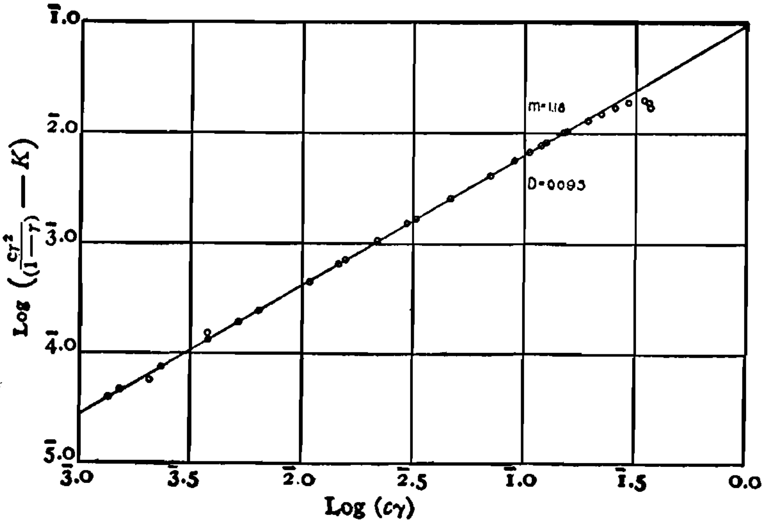

FIG. 9. $M - D$ Plot for KNH_2 in NH_3.

that the points lie upon a straight line well within the limits of experimental error. This plot yields a value of $D = 0.095$ and $m = 1.18$. Finally, in order to obtain a more precise value of K, values of K' are

[5] Kraus and Bray, *loc. cit.*

plotted against the values of the ion concentration to the power 1.18. This plot is shown in Figure 10. The value for D in this case is not altered from that originally determined, but the value of K is altered from 1.26 to 1.20.

It will be observed that, throughout, the points lie upon a straight line within the limits of experimental error. The equation connecting

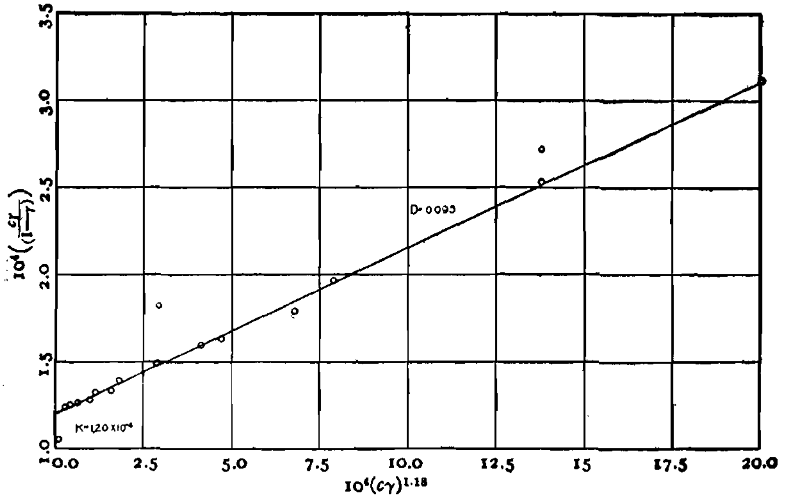

FIG. 10. $K-D$ Plot for KNH_2 in NH_3.

the equivalent conductance with the concentration for solutions of potassium amide in liquid ammonia is, therefore:

$$K' = \frac{(C\gamma)^2}{C(1-\gamma)} = 0.095(C\gamma)^{1.18} + 1.20 \times 10^{-4}$$

where $\gamma = \dfrac{\Lambda}{301}$.

The calculated values are compared with the experimental values in Figure 11, where the equivalent conductances are plotted as ordinates against the logarithms of the concentrations as abscissas. It will be observed that the calculated curve corresponds with the experimental curve up to a concentration of approximately 2 normal. Beyond this concentration the experimental curve departs rapidly from the calculated curve. As we shall see presently, at higher concentrations, the viscosity of the solutions increases very largely and it is therefore not possible to test the applicability of the equation at these concentrations.

It becomes a matter of interest to determine whether an equation of

this type is generally applicable to solutions of electrolytes in various solvents. Since a larger amount of experimental material is available for solutions in liquid ammonia than for solutions in any other solvent, we may consider solutions in this solvent first. Since the more dilute solutions have already been considered and found to conform to the

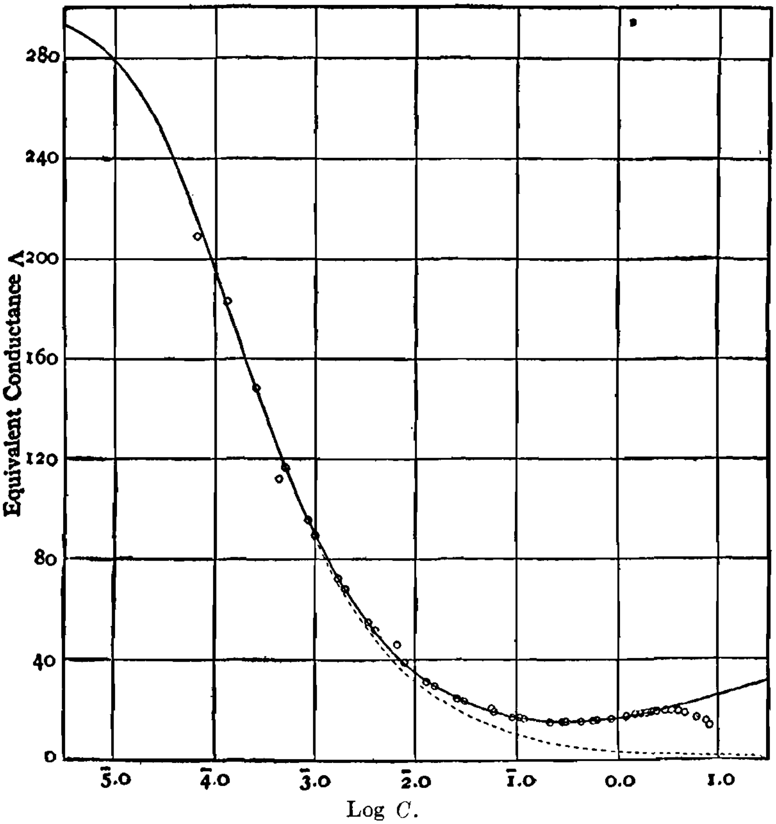

FIG. 11. Comparison of Experimental Values with Equation 11 for KNH_2 in NH_3.

mass-action law as a limiting form, it follows that the equation will be applicable to the more dilute solutions in any case. It remains, therefore, to determine whether the equation likewise applies to the more concentrated solutions.

Kraus and Bray,[6] who have examined the applicability of this equation to a large number of non-aqueous solutions, including solutions in ammonia, have concluded that the experimental values may be repre-

[6] Kraus and Bray, *loc. cit.*

sented by an equation of this type within the limits of experimental error. In general, it has been found that the more consistent the experimental data are among themselves, the more nearly do they adjust themselves to Equation **11**. The results for inorganic electrolytes dissolved in ammonia are summarized in Table XXVII.

TABLE XXVII.

CONSTANTS OF THE CONDUCTANCE FUNCTION FOR INORGANIC ELECTROLYTES IN NH_3 AT $-33°$.

Electrolyte	$10^4 K$	m	D
KNH_2	1.20	1.18	0.095
AgI	2.90	0.70	0.009
NH_4Cl	12.0	0.84	0.127
KNO_3	15.5	0.96	0.25
$NaNO_3$	23.0	0.89	0.32
NH_4Br	23.0	0.82	0.24
$LiNO_3$	26.0	0.86	0.34
NaI	28.0	0.83	0.43
$AgNO_3$	28.0	0.83	0.36
NH_4NO_3	28.0	0.86	0.39
KI	42.0	0.94	0.62

The values of Λ_0 are not given in this table, but they will be found in Table XXII. By means of the constants in these tables the equivalent conductances of the various electrolytes may be calculated at any desired concentration within the limits of experimental error up to approximately normal concentrations. It is obvious that a comparison of the ionization of different electrolytic solutions may be made by means of the constants given above. The relative ionization of two salts will vary as a function of the concentration, since the constants for the two electrolytes will not, as a rule, have the same value. The values of the constant K have already been considered and need not be further discussed here. The values of the constant D are seen to lie within fairly narrow limits. Excepting the constants for potassium amides and silver iodide, the values of D lie between 0.127 and 0.62, and most of the values lie between 0.24 and 0.43. There is no fixed relation between the values of D and of K, although in general an electrolyte with a large value of K has a large value of D. Thus, potassium amide, silver iodide and ammonium chloride have the smallest values of K and likewise they have the smallest values of the constant D. So, also, potassium iodide, which has the highest value of the constant K, likewise has the highest value of the constant D. Apparently, the constants K and D are not

entirely independent of each other, or, in other words, they depend in a corresponding manner upon some property of the electrolyte. The values of m lie between 0.70 and 1.18 and, for the most part, they lie between 0.82 and 0.96. The general form of the curve, as we shall presently see, is determined largely by the value of the constant m. It follows, consequently, that the curves for the various electrolytes will in general be similar. No definite relation appears to exist between the values of the constant m and the constants D and K. In many cases, however, as we shall see later, electrolytes having a small value of K and D have a relatively large value of m. Silver iodide is an exception to this rule.

The constants for a number of organic electrolytes are given in Table XXVIII.

TABLE XXVIII.

CONSTANTS OF EQUATION 11 FOR ORGANIC ELECTROLYTES IN NH_3 AT —33°.

Solute	Λ_0	$10^4 K$	m	D
Cyanacetamide	260	0.045	1.24	0.026
Benzenesulphonamide	208	1.39	1.00	0.029
Methylnitramine	256	8.4	0.85	0.080
Metanitrobenzenesulphonamide	231	12.5	0.76	0.103
Nitrourethaneammonium	262	21.6	0.76	0.22
Trinitraniline	234	30.0	0.73	0.38

They have been arranged in the order of increasing values of K. It is at once evident that there is no relation between the various constants and the value of Λ_0. On the other hand, there is apparently a rough parallelism between the constants K and D. The order of the K and D constants, in other words, is identical. The order of the constant m appears to be the reverse of that of the constants D and K; that is, as K and D increase, m decreases.

Aside from solutions in liquid ammonia, the equation has been found to hold for solutions in sulphur dioxide,[7] amyl and propyl[8] alcohols and phenol.[9] In the case of the sulphur dioxide solutions the equation holds within the limits of experimental error. In that of the alcohol solutions, the deviations appear to be considerable at certain points, but it is possible that these are due either to experimental errors or to a lack of proper adjustment of the constants. The constants found are as follows:

[7] Kraus and Bray, *loc. cit.*
[8] Keyes and Winninghoff, *J. Am. Chem. Soc.* 38, 1178 (1916).
[9] Kurtz, Thesis, Clark University (1921).

TABLE XXIX.

CONSTANTS OF EQUATION 11 FOR SOLUTIONS IN DIFFERENT SOLVENTS.

Solvent	Solute	m	K	D	Λ_0
Sulphur dioxide	KI	1.14	8.5×10^{-4}	0.403	207.
Iso-amyl alcohol	NaI	1.2	5.85×10^{-4}	0.374	7.79
Propyl alcohol	NaI	0.75	38.3×10^{-4}	0.208	20.1
Phenol	$(CH_3)_4NI$	1.28	2.3×10^{-4}	0.69	16.67

Comparing the ionization in ammonia and sulphur dioxide, in view of the much lower value of the constant K, dilute solutions in sulphur dioxide are ionized to a much smaller extent than are solutions in ammonia. On the other hand, in the more concentrated solutions, the ionization values again approach each other, since the value of D for sulphur dioxide is relatively large and the value of m is much greater than that in ammonia. The conductance curves of solutions in sulphur dioxide, phenol and amyl alcohol pass through a minimum while that of solutions in propyl alcohol resembles the curve for aqueous solutions.

In the case of a great many solutions whose ionization is relatively low, the limiting value of the equivalent conductance in dilute solutions cannot be determined. Under these conditions, the value of K remains indeterminate. Nevertheless, if the ionization is relatively low, the applicability of Equation 11 may be tested approximately. It is apparent that, when the ionization is low, the constant K becomes negligible in comparison with the term involving the constant D. Also, the value of Λ becomes small in comparison with that of Λ_0, so that for purposes of approximation the value of Λ may be neglected in comparison with that of Λ_0. Under these conditions Equation 11 reduces to the form:

$$C\Lambda^2 = D\Lambda_0^{2-m}(C\Lambda)^m. \tag{12}$$

For the sake of brevity we may write:

$$D\Lambda_0^{2-m} = P. \tag{13}$$

If we take the logarithm of both sides of this equation, we obtain the linear equation:

$$\log C\Lambda^2 = m \log C\Lambda + \log P. \tag{14}$$

In order to test the applicability of the equation to solutions of very low ionization, therefore, it is only necessary to plot the logarithms of the values of $C\Lambda$ and of $C\Lambda^2$, both of which may be obtained from experimental data. If the equation holds, the points will lie upon a straight

line, the slope of which gives the value of the constant m and the intercept on the axis of $C\Lambda^2$ the value of P.

In Figure 12 are shown plots of Equation 14 for a number of organic electrolytes dissolved in hydrobromic and in hydriodic acids and in

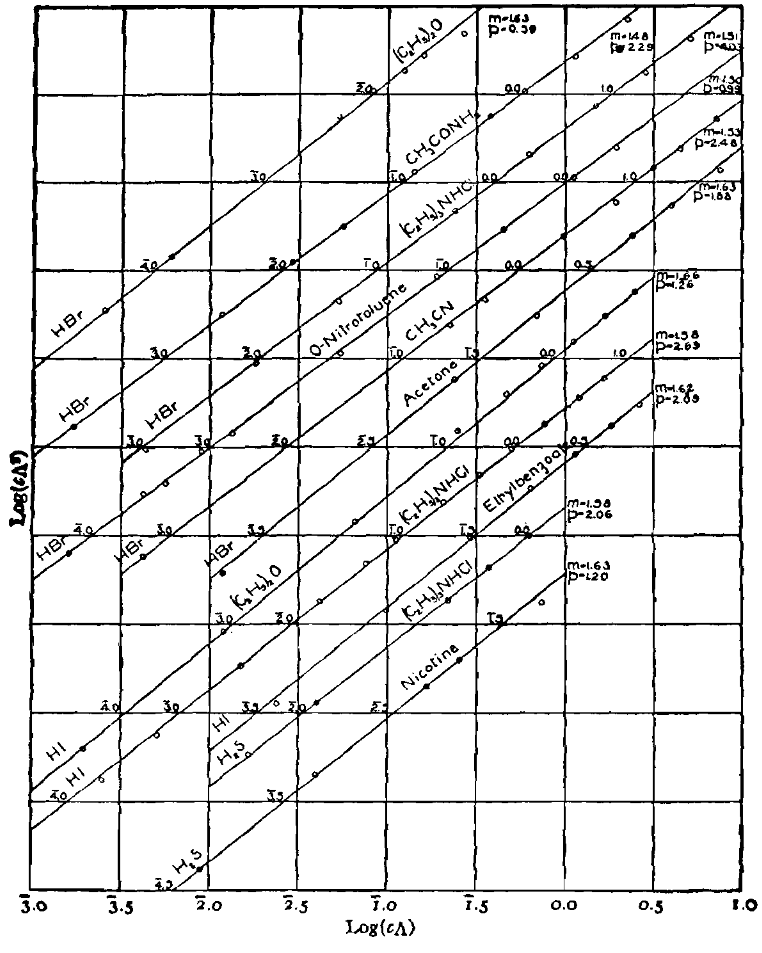

Fig. 12. Illustrating the Applicability of Equation 11 to Solutions of Binary Electrolytes in Solvents of Low Dielectric Constant.

hydrogen sulfide. These solutions are well adapted to the purpose of testing the applicability of the equation, since the ionization of electrolytes in these solvents is extremely low. It is evident that, except in the case of a few very concentrated solutions, the equation holds within the limits of experimental error. The curves, in general, have approximately

the same slope, which follows from the fact that the value of m is approximately the same for these solutions. The greater the value of the exponent m, the steeper the curve on the plot. A great many solutions of this type have been measured and the results have been compared with the equation. The deviation in no case appears to be very great, from which it may be concluded that the equation holds to a considerable degree of approximation. The values of the constants m and P for various solutions are given in Table XXX.[10]

Many of the substances which appear in this table are not ordinarily classed as typical electrolytes. They are, in general, basic compounds

TABLE XXX.

VALUES OF THE CONSTANTS OF EQUATION 12 FOR VARIOUS SOLUTIONS.

Liquid Hydrochloric Acid (HCl).

Solute	Formula	Temperature	m	P
Triethylammonium chloride	$(C_2H_5)_3N.HCl$	—100°	1.42	5.75
Acetamide	CH_3CONH_2	—100°	1.40	5.53
Methylcyanide	CH_3CN	—100°	1.44	4.17
Resorcinol	$C_6H_4(OH)_2$	—89°	1.18	3.89
Hydrocyanic acid	HCN	—100°	1.46	3.33
Toluic acid	$CH_3.C_6H_4COOH$	—96°	1.52	1.58
Diethylether	$(C_2H_5)_2O$	—100°	1.51	1.38
Propionic acid	C_2H_5COOH	—96°	1.47	1.21
Acetic acid	CH_3COOH	—96°	1.42	1.09
Benzoic acid	C_6H_5COOH	—96°	1.42	0.94
Butyric acid	C_3H_7COOH	—96°	1.45	0.85
Methylalcohol	CH_3OH	—89°	1.61	0.71
Formic acid	HCOOH	—96°	1.55	0.67
Ethylalcohol	C_2H_5OH	—89°	1.70	0.50
Butylalcohol	C_4H_9OH	—89°	1.62	0.38

Liquid Hydrobromic Acid (HBr).

Solute	Formula	Temperature	m	P
Triethylammonium chloride	$(C_2H_5)_3N.HCl$	—81°	1.51	4.03
Thymol	$CH_3.C_3H_7.C_6H_3OH$	—80°	1.57	3.60
Methylcyanide	CH_3CN	—81°	1.53	2.48
Acetamide	CH_3CONH_2	—81°	1.48	2.29
Acetone	$(CH_3)_2CO$	—81°	1.63	1.88
Metacresol	m-$CH_3.C_6H_4OH$	—80°	1.54	1.70
Orthonitrotoluene	o-$CH_3.C_6H_4NO_2$	—81°	1.50	0.99
Benzoic acid	C_6H_5COOH	—80°	1.67	0.82
Acetic acid	CH_3COOH	—80°	1.66	0.78

[10] Kraus and Bray, *loc. cit.*

TABLE XXX.—*Continued.*

Liquid Hydrobromic Acid (HBr).

Solute	Formula	Temperature	m	P
Metatoluic acid	$m\text{-}CH_3.C_6H_4COOH$	—80°	1.65	0.77
Paratoluic acid	$p\text{-}CH_3.C_6H_4COOH$	—80°	1.62	0.76
Butyric acid	C_3H_7COOH	—80°	1.66	0.71
Orthotoluic acid	$o\text{-}CH_3C_6H_4COOH$	—80°	1.60	0.65
Diethylether	$(C_2H_5)_2O$	—81°	1.63	0.59
Paracresol	$p\text{-}CH_3.C_6H_4OH$	—80°	1.66	0.55
Resorcinol	$C_6H_4(OH)_2$	—80°	1.40	0.52
Orthocresol	$o\text{-}CH_3.C_6H_4OH$	—80°	1.68	0.45
Methylalcohol	CH_3OH	—80°	1.80	0.41
Allylalcohol	$C_2H_3.CH_2OH$	—80°	1.79	0.39
Ethylalcohol	C_2H_5OH	—80°	1.80	0.35
Amylalcohol	$C_5H_{11}OH$	—80°	1.84	0.27
Normal propylalcohol	$n\text{-}C_3H_7OH$	—80°	1.77	0.27
Phenol	C_6H_5OH	—80°	1.61	0.27

Liquid Hydriodic Acid (HI).

Solute	Formula	Temperature	m	P
Triethylammonium chloride	$(C_2H_5)_3N.HCl$	—50°	1.58	2.69
Ethylbenzoate	$C_6H_5COOC_2H_5$	—50°	1.62	2.09
Diethylether	$(C_2H_5)_2O$	—50°	1.66	1.26

Liquid Hydrogen Sulfide (H_2S).

Solute	Formula	Temperature	m	P
Triethylammonium chloride	$(C_2H_5)_3N.HCl$	—81°	1.58	2.06
Nicotine	$C_{10}H_{14}N_2$	—81°	1.63	1.20

Mercuric Chloride ($HgCl_2$).

Solute	Formula	Temperature	m	P
Caesium chloride	$CsCl$	282°	1.20	14.5
Potassium chloride	KCl	282°	1.21	14.3
Ammonium chloride	NH_4Cl	282°	1.22	14.3
Sodium chloride	$NaCl$	282°	1.29	13.7
Cuprous chloride	$CuCl$	282°	1.33	13.6

Liquid Iodine (I_2).

Solute	Formula	Temperature	m	P
Potassium iodide	KI	140°	1.44	13.5

Ethylamine ($C_2H_5NH_2$).

Solute	Formula	Temperature	m	P
Silver nitrate	$AgNO_3$	0°	1.42	4.68
Ammonium chloride	NH_4Cl	0°	1.57	1.97
Lithium chloride	$LiCl$	0°	1.54	1.80

Amylamine ($C_5H_{11}NH_2$).

Solute	Formula	Temperature	m	P
Silver nitrate	$AgNO_3$	25°	1.67	1.97

TABLE XXX.—*Continued.*

Aniline ($C_6H_5NH_2$).

Solute	Formula	Temperature	*m*	*P*
Ammonium iodide	NH_4I	25°	1.44	2.19
Silver nitrate	$AgNO_3$	25°	1.42	2.02
Pyridine hydrobromide	$C_5H_5N.HBr$	25°	1.51	1.91
Aniline hydrobromide	$C_6H_5NH_2.HBr$	25°	1.44	1.29
Lithium iodide	LiI	25°	1.33	1.04
Methyl Aniline ($C_6H_5NHCH_3$).				
Pyridine hydrobromide	$C_5H_5N.HBr$	25°	1.64	1.19
Aniline hydrobromide	$C_6H_5NH_2.HBr$	25°	1.59	0.59
Acetic Acid (CH_3COOH).				
Lithium bromide	LiBr	25°	1.43	2.60
Pyridine	C_5H_5N	25°	1.56	1.86
Dimethylaniline	$C_6H_5N(CH_3)_2$	25°	1.48	1.53
Aniline	$C_6H_5NH_2$	25°	1.52	1.32
Propionic Acid (C_2H_5COOH).				
Lithium bromide	LiBr	25°	1.74	0.84
Aniline	$C_6H_5NH_2$	25°	1.79	0.37
Pyridine	C_5H_5N	25°	1.76	0.32
Bromine (Br_2).				
Trimethylammoniumchloride[11]	$(CH_3)_3NHCl$	18°	1.62	0.55
Iodine[12]	I_2	25°	1.74	0.17

containing either oxygen or nitrogen and in all likelihood they owe their electrolytic properties to the formation of complexes with the solvent, in which oxygen and nitrogen exhibit basic properties. For a given value of *m* the ionization is in general the greater the greater the value of *P*. It is apparent that among these electrolytes the typical salts are the most highly ionized. In solutions in the halogen acids and hydrogen sulphide, the substituted ammonium salts, or their derivatives, are more highly ionized than are other substances. In general, also, the typical salts have values of the constant *m* smaller than those of electrolytes which have a lower ionization. There are, however, a few exceptions, such, for example, as resorcinol in hydrochloric acid, which has a value

[11] Darby, *J. Am. Chem. Soc.* *40*, 347 (1918).
[12] Plotnikow and Rokotjan, *Ztschr. f. phys. Chem.* *84*, 365 (1913).

of m of only 1.18. Correspondingly, resorcinol in hydrobromic acid has a constant of only 1.40, which is distinctly lower than that of other substances dissolved in this solvent. It is interesting to note that the value of the constant m never exceeds 2. The highest value of this constant is 1.80 for methyl and ethyl alcohols in hydrobromic acid. It appears probable that the values of m for these two substances in hydrogen iodide will be found greater than in hydrogen bromide.

In fused mercuric chloride the different typical salts exhibit a very similar behavior. The constant P differs only inappreciably for different electrolytes and the values of the constant m, for the most part, fall within very narrow limits.

In the amines the constant m increases and the constant P decreases as the organic radical becomes more complex. The same is true in the case of acetic and propionic acids, where the constant m for propionic acid is much greater than for acetic acid. Judging by the relatively low value of the constant m for liquid iodine, this substance is a fairly good ionizing agent.

2. *Geometrical Interpretation of the Conductance Function.* The conductance function:

$$K' = \frac{C\gamma^2}{1-\gamma}$$

may be interpreted most readily by graphical methods. It will be understood that $\gamma = \frac{\Lambda}{\Lambda_0}$ and that the following equations may at once be converted to equations in which $C\Lambda$ and Λ appear as variables in place of $C\gamma$ and γ. In speaking of the ionization, it is not intended to convey the impression that the conductance ratio necessarily measures the ionization, but rather it is introduced as a convenient variable for the purpose of discussion. If we differentiate the above equation, we have:

$$\text{(15)} \qquad \frac{d\gamma}{d(C\gamma)} = \frac{\gamma^2}{K'}\left(\frac{C\gamma}{K'}\,\frac{dK'}{d(C\gamma)} - 1\right).$$

The coefficient $\frac{d\gamma}{d(C\gamma)}$, which is the tangent to the γ, $C\gamma$-curve, is a measure of the change of the ionization as a function of the ion concentration at any point on the curve. It is evident that if the term $\frac{C\gamma}{K'}\,\frac{dK'}{d(C\gamma)}$ approaches zero as $C\gamma$ approaches zero, the tangent will approach the value $-\frac{1}{K}$ as a limit, where K is the limit which K' ap-

proaches at zero concentration. At higher concentrations the tangent will decrease; that is, the ionization will increase less rapidly for a given increase in the ion concentration, because both K' and $\frac{C\gamma}{K'}\frac{dK'}{d(C\gamma)}$ increase with the concentration.

If we introduce Λ and $C\Lambda$ as variables, Equation 15 has the form:

$$\frac{d\Lambda}{d(C\Lambda)}=\frac{\Lambda^2}{\Lambda_0{}^2K'}\left(\frac{C\Lambda}{K'}\,\frac{dK'}{d(C\Lambda)}-1\right). \tag{16}$$

The plot of Λ against the specific conductance in dilute solution will therefore be a curve convex toward the axis of specific conductances, and as the concentration decreases it will approach a line whose tangent is $-\frac{1}{K}$, provided the conditions mentioned in the preceding paragraph are fulfilled.

In order to follow up the form of the curve at higher concentrations, we may introduce the conductance function 11. On differentiating this function we have:

$$\frac{d\Lambda}{d(C\Lambda)}=\frac{\Lambda^2}{\Lambda_0K'}\left(m-1-\frac{mK}{K'}\right). \tag{17}$$

Since K' approaches K at low concentrations, it follows that the tangent approaches the value $-\frac{1}{K}$ as a limit. At higher concentrations, the tangent decreases, since K' decreases. Ultimately the form of the curve depends upon the value of m. If m is less than 1, then the tangent will always have a negative value; in other words, the equivalent conductance will always decrease with increasing values of the specific conductance. On the other hand, when m is greater than unity, the tangent will become zero, when:

$$m-1-\frac{mK}{K'}=0; \tag{18}$$

that is, at this point the conductance passes through a minimum value after which it increases with increasing values of the specific conductance. Introducing for K' its value, $D\left(\frac{C\Lambda}{\Lambda_0}\right)^m+K$, and denoting by C' and Λ' the values of the concentration and the equivalent conductance at the minimum point, we have:

$$\left(\frac{C'\Lambda'}{\Lambda_0}\right)=\frac{K}{D(m-D)}=(C'\gamma')^m, \tag{19}$$

where $\gamma' = \frac{\Lambda'}{\Lambda_0}$. This equation gives the value of the specific conductance or the ion concentration, at the minimum point. The value of the ionization follows from the equation:

$$\frac{\gamma'}{1-\gamma'} = \frac{D(C'\gamma') + K}{C'\gamma'}. \tag{20}$$

When m equals 1, we have a limiting case in which Equation 18 reduces to:

$$\frac{d\Lambda}{d(C\Lambda)} = \frac{\Lambda^2}{\Lambda_0^2 K'} \quad \frac{mK}{K'}. \tag{21}$$

It is evident that since $\frac{K}{K'}$ decreases as the concentration increases, the tangent approaches a value zero at high concentration. The ionization, therefore, approaches a constant value which may be obtained by writing $m = 1$ in Equation 11; we have:

$$C\gamma'' \frac{\gamma''}{1-\gamma''} = D(C\gamma'') + K$$

or, neglecting K,

$$\frac{\gamma''}{1-\gamma''} = D \quad \text{or} \quad \gamma'' = \frac{D}{1+D}. \tag{22}$$

The ionization of such solutions, therefore, approaches the value $\frac{D}{1+D}$ as a limit. If an electrolyte has a very small value of K and a relatively large value of D, while the value of m is nearly unity, the conductance will vary only very little with concentration at higher concentrations. This is the case with the cyanides in liquid ammonia, more particularly with the cyanides of gold and silver. The value of m is a little less than unity for the first substance and a little greater than unity for the second.[13] For the ion concentration $C\gamma = 1$, Equation 11 reduces to:

$$\frac{\gamma_1}{1-\gamma_1} = D + K,$$

and since K may be neglected at this concentration, we have:

$$\frac{\gamma_1}{1-\gamma_1} = D. \tag{23}$$

The constant D, therefore, measures the ratio of the ionized to the unionized fraction at the concentration $C\gamma = 1$. We shall see that, for a

[13] Kraus and Bray, *loc. cit.*, p. 1360.

given substance in different solvents or in the same solvent at different temperatures, the value of D is practically constant, while the values of m and K vary. It follows, therefore, that the γ, $C\gamma$-curves for all such solutions pass through the point $C\gamma = 1$, $\gamma = \frac{D}{D+1}$. This relation is of importance in interpreting the influence of temperature on the conductance of solutions.

The further discussion of the relation between the conductance and the concentration is greatly simplified by introducing the function K' and examining the manner in which K' varies as a function of the ion concentration. Differentiating, we have the equations:

(24)
$$\frac{dK'}{d(C\Lambda)} = \frac{Dm(C\Lambda)^{m-1}}{\Lambda_0^m}$$
or
$$\frac{dK'}{d(C\gamma)} = Dm(C\gamma)^{m-1}$$

If D were zero, that is, if the mass-action law held, we should have:

(25)
$$\frac{dK'}{d(C\gamma)} = 0$$
or $K' =$ constant.

On the other hand, when the D term is present, K' will always increase with the concentration. The form of the K', $C\Lambda$-curve is determined mainly by the constant m. When $m = 1$, we evidently have:

(26)
$$\frac{dK'}{d(C\gamma)} = Dm \quad \text{or} \quad \frac{dK'}{d(C\Lambda)} = \frac{Km}{\Lambda_0^m}.$$

In this limiting case, therefore, K' varies as a linear function of the specific conductance $C\Lambda$.

The form of the curves for values of m greater and less than unity may readily be determined by means of the second differential coefficients. We have:

(27)
$$\frac{d^2K'}{d(C\gamma)^2} = Dm(m-1)\ (C\gamma)^{m-1}.$$

When $m < 0$,

(28)
$$\frac{d^2K'}{d(C\gamma)^2} < 0$$

and the K, $C\gamma$-curve is everywhere concave toward the axis of $C\gamma$. When $m > 1$,

$$(29) \qquad \frac{d^2K'}{d(C\gamma)^2} > 0$$

and the curve is everywhere convex toward the $C\gamma$-axis. In the limiting case, $m = 1$, and

$$(30) \qquad \frac{d^2K'}{d(C\gamma)^2} = 0,$$

and K is a linear function of $C\gamma$.

From Equation 24, it follows that when $m < 1$,

$$(31) \qquad \lim_{c=0} \frac{dK'}{d(C\Lambda)} = \infty$$

and when $m > 1$,

$$(32) \qquad \lim_{c=0} \frac{dK'}{d(C\Lambda)} = 0.$$

In the first case the K', $C\gamma$-curve approaches the limit K asymptotic to the axis of K', while in the second case it approaches the limit asymptotic to a line parallel to the axis of $C\gamma$.

The curvature of both curves increases as the concentration decreases.[14] For the radius of curvature of the K', $C\gamma$-curve we have the equation:

$$(33) \qquad R^{2/3} = \frac{(C\gamma)^{\frac{2(2-m)}{3}}}{[Dm(m-1)]^{3/2}} + \frac{m^{4/3}\,D^{4/3}\,(C\gamma)^{\frac{2(2m-1)}{3}}}{(m-1)^{2/3}}$$

The exponent $2-m$ of the first term of the right-hand member of this equation is positive for all values of m less than 2. Since no solutions are known for which m is greater than 2, we need not consider greater values of m. It is evident, therefore, that, due to the first term, the radius of curvature increases with $C\gamma$ for all values of m. For $m > 1$, the coefficient $2m - 1$ is positive and the radius of curvature increases with $C\gamma$ due to this term also. When $m < 1$, $2 - m > 2m - 1$ so long as m is greater than zero. It follows, therefore, that the first term overbalances the second and that the curvature, for all values of m between zero and 2, decreases with increasing concentration, becoming infinite in the limit. For $m = 1$, $R = \infty$, and the curvature is zero. For $m < 1$, the curvature is negative; that is, the curve is concave toward the $C\gamma$-axis. While for $m > 1$, the curvature is positive, and the curve is convex toward this axis.

For given values of D and K and for different values of m we have a family of curves passing through the points $C\gamma = 0$, $K' = K$ and $C\gamma = 1$, $K' = D + K$. Such a system of curves is shown in Figure 13. The con-

[14] Kraus, *J. Am. Chem. Soc.* 42, 6 (1920).

stants assumed are: $D = 1.703$, $K = 0.001$, and $\Lambda_0 = 129.9$ for all curves, while $m = 0.52$ for Curve I, $m = 1.50$ for Curve II, and $m = 1$ for Curve III. The greater the value of m, the less rapidly does K' increase at the lower concentrations. For a value of $m = 0$, the curve degenerates into a horizontal straight line, corresponding to the mass-action constant $K' = K + D$.

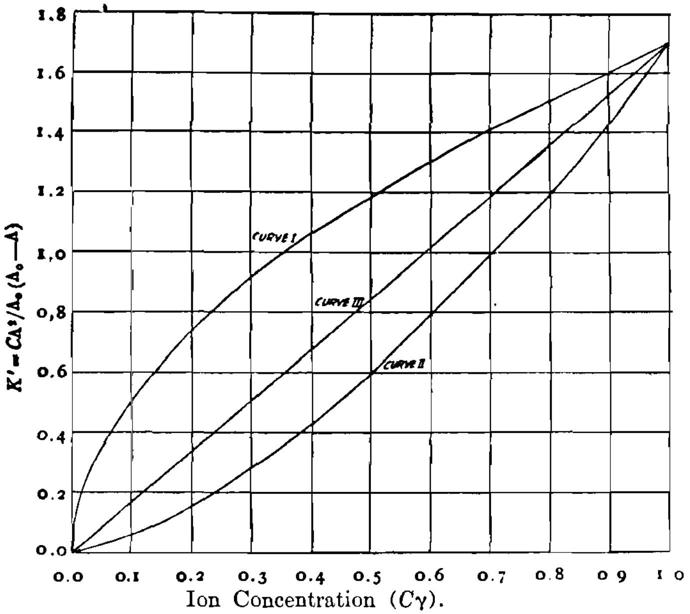

FIG. 13. Showing Typical K' Curves for Different Values of m According to Equation 11.

It is evident that a given percentage deviation of K' with respect to K will be found at different values of the ion concentration. If we consider two solutions for which the value of K' has increased by a given percentage amount over K in both cases, then the ion concentrations of the two solutions are related according to the equation:

$$\frac{(C_1\gamma_1)^{m_1}}{(C_2\gamma_2)^{m_2}} = \frac{\dfrac{D_2}{K_2}}{\dfrac{D_1}{K_1}} \tag{34}$$

If D/K for the two solutions is of the same order, then the ratio of the ion concentrations will depend upon the values of m. The smaller the value of m, the lower will be the ion concentration at which a given change in K will be found. This is also obvious from Figure 13. For

a given rise in the curve above the value of K, the ion concentration will be the smaller, the smaller the value of m. The value of the ion concentrations corresponding to any given value of K' are found by drawing a horizontal line and reading off the concentrations at the points of intersection. In Table XXXI are given the values of m, D/K, and the ion

TABLE XXXI.

VALUE OF D/K AND OF m AND CONCENTRATIONS AT WHICH GIVEN DEVIATIONS FROM THE MASS-ACTION LAW OCCUR FOR SOLUTIONS IN NH_3.

Electrolyte	$D/K \times 10^{-2}$	m	$\frac{K'-K}{K}=5\%$		$\frac{K'-K}{K}=20\%$	
			$C\gamma \times 10^4$	$C \times 10^4$	$C\gamma \times 10^4$	$C \times 10^4$
KNH_2	7.91	1.18	2.76	8.82	8.97	65.0
AgI	0.345	0.70	0.86	1.14	6.38	18.03
NH_4Cl	1.06	0.84	1.10	1.19	5.70	7.99
KNO_3	1.35	0.89	1.35	1.46	6.89	10.80
$NaNO_3$	1.39	0.89	1.33	1.42	6.52	8.06
NH_4Br	1.04	0.82	0.89	0.92	4.85	5.70
$LiNO_3$	1.31	0.86	1.06	1.10	5.33	6.32
NaI	1.54	0.83	0.63	0.64	3.33	3.66
$AgNO_3$	1.29	0.83	0.78	0.80	3.38	3.80
NH_4NO_3	1.39	0.86	0.98	1.02	4.92	5.64
KI	1.43	0.94	2.03	2.12	8.91	10.50
Cyanacetamide	55.8	1.24	0.83	15.4	2.53	120.0
Benzenesulphonamide	2.09	1.00	2.40	6.34	9.59	64.8
Methylnitramine	0.941	0.85	1.32	1.52	7.08	12.04
Metanitrobenzenesulphonamide	0.825	0.76	0.58	0.61	3.62	4.49
Nitrourethaneammonium	1.02	0.76	0.44	0.45	2.74	3.03
Trinitraniline	1.27	0.73	0.22	0.22	1.45	1.49

concentrations $C\gamma$ and the total salt concentrations at which the increase over the values of K amounts to 5 and 20 per cent respectively.

For approximately the same value of D/K the value of $C\gamma$, for which a given increase occurs in the value of the mass-action function, decreases as m decreases. Thus, in the case of benzenesulphonamide, methylnitramine, metanitrobenzenesulphonamide, and trinitraniline, the value of m decreases from 1.0 to 0.73, while the value of $C\gamma$ for a 5% increase in the function decreases from 2.40 to 0.22. Similarly, in the case of sodium and potassium iodides, the values of m are respectively 0.83 and 0.94, and the values of the ion concentrations for a 5% increase in the function are 0.63 and 2.03 respectively. The deviations from the simple mass-action law, at a given concentration therefore appear smaller in the case of potassium iodide than in that of sodium iodide. For the same

value of the constant m, a given deviation occurs at the lower concentration, the greater the value of D/K. Thus, sodium iodide and silver nitrate both have a value of the exponent $m = 0.83$, while the values of D/K are 1.54 and 1.29 respectively. Correspondingly, the values of the ion concentrations for a 5% increase of the function are 0.63 and 0.78 respectively. The value of D/K for typical electrolytes in ammonia lies in the neighborhood of 100. For weak electrolytes the value of D/K appears to be larger, as for example for cyanacetamide and potassium amide. In the case of silver iodide, however, which appears to be a very exceptional electrolyte, the value of D/K is extremely small. As we shall see below, the value of D for a given electrolyte is relatively independent of the nature and condition of the solvent. At higher temperatures, the dielectric constant of the solvent decreases and with it there is a large decrease in the value of the constant K, while the constant D remains practically fixed. At higher temperatures, therefore, the value of D/K will increase. This tends to increase the deviations from the simple mass-action relation. On the other hand, the value of m increases with increasing temperature and decreasing dielectric constant, and this tends to make the percentage deviations from the simple mass-action relation smaller. The observed effect will be the resultant of these two. From the known form of the conductance curve in solvents of very low dielectric constant, it is evident that ultimately the effect due to the increase in the value of D/K overbalances that due to the increase in the value of m.

Corresponding to the K', $C\gamma$-curves, we have the γ, $C\gamma$-curves. These curves pass through the common points $\gamma = 1$, $C\gamma = 0$, and $\gamma = \frac{D+K}{1+D+K}$ and $C\gamma = 1$.

The particular case when the value of m is equal to unity, which leads to a linear relation between the function K' and the ion concentration, likewise yields a very simple relation between the equivalent conductance and the specific conductance. In this case we may write our equation:

$$\frac{\gamma}{1-\gamma} = D + \frac{K}{C\gamma}$$

$$\text{(35)} \qquad \text{or} \quad \frac{\Lambda}{\Lambda_0 - \Lambda} = D + \frac{K\Lambda_0}{C\Lambda}.$$

It is obvious that the ratio $\frac{\Lambda}{\Lambda_0 - \Lambda}$, or what is proportional to it, the ratio $\frac{\gamma}{1-\gamma}$, is now a linear function of the reciprocal of the specific conduct-

ance or of the ion concentration. The equation obviously approaches in form that which follows from the mass-action law which is:

$$\frac{\gamma}{1-\gamma}=\frac{K}{C\gamma}. \tag{36}$$

If the mass-action law holds, the ratio of the ionized to the un-ionized fraction is inversely proportional to the ion concentration. If, therefore, we were to plot the values of the ratio $\frac{\gamma}{1-\gamma}$ against values of the ion concentration $C\gamma$, we should obtain a rectangular hyperbola. When the constant m equals unity, the equation is of the same form, except that the entire curve is raised by an amount equal to D. In this case, therefore, the curve is again a rectangular hyperbola asymptotic to the $\frac{\gamma}{1-\gamma}$ axis on one side and asymptotic to the horizontal line $\frac{\gamma}{1-\gamma}=D$ on the other.

In very concentrated solutions, in the case of substances for which the value of m does not differ too greatly from unity, the equivalent conductance at a given concentration for different electrolytes is roughly proportional to the value of D. The value of this constant, as has already been pointed out, is in a large measure a distinctive property of the electrolyte and varies only little as a function of the solvent. For the strongest electrolytes the value of D is always of the same order.

As we shall see later, the conductance of an electrolyte is a function of the temperature. At very high and very low concentrations the conductance invariably increases with increasing temperature, while, at intermediate concentrations, the conductance in many cases decreases with increasing temperature, and always decreases at high temperatures. As we shall see, this behavior is due to the fact that the value of D remains constant and independent of the temperature, while the constant m varies, increasing with increasing temperature. At intermediate concentrations, therefore, the ionization decreases with increasing temperatures whereas at very high and very low concentrations the ionization remains practically fixed.

3. *Relation between the Properties of Solvents and Their Ionizing Power.* Various attempts have been made to connect the power of a solvent to ionize dissolved substances with the properties of this solvent. So, for example, it has been suggested that those solvents which are normally associated are capable of dissociating substances dissolved in them. This relation, however, is not a general one for it is now known

that all liquid substances are capable of ionizing substances dissolved in them quite irrespective of what their properties may be. The only condition necessary in order that the solution shall conduct the current is that the electrolyte shall be sufficiently soluble so that a highly concentrated solution may be obtained. We have seen, in the preceding section, that in solvents which have a low ionizing power the conductance decreases with decreasing concentration, and appears to approach a value of zero. If the electrolyte, therefore, is not very soluble, its influence on the conductance of the solvent will be inappreciable. If, however, an electrolyte is soluble up to concentrations as high as normal, then its solutions will in all cases be found to conduct the current. In general, the typical inorganic electrolytes are not soluble in weak ionizing agents, but certain organic electrolytes, such as the salts of organic bases, are quite soluble and yield solutions which conduct the current. It is probable that all liquid dielectric media to some extent possess the power of ionizing substances dissolved in them.

The difference between the properties of solutions of electrolytes in different solvents does not consist in a power to ionize an electrolyte in one case and the entire absence of this power in another, but rather in a difference in the form of the conductance curve which varies with the nature of the solvent, either with its constitution or with its temperature. That property of the solvent which appears to control the form of the conductance curve is the dielectric constant. Thomson [15] and Nernst [16] first suggested that the ionizing power of a solvent is determined by its dielectric constant. This constant, however, is by no means to be taken as a measure of the ionizing power of a solvent, for the ionization curve of a given electrolyte is a complex function of the concentration and the relative ionizations will vary with the concentration. At very high concentrations the relative ionizations will, in general, differ much less than at low concentrations. Indeed, in the preceding section we saw that the constant D determines the ionization at very high concentrations and that, therefore, for a given electrolyte in different solvents there is a certain concentration at which the ionization of this electrolyte will be practically the same in all solvents. What we must expect to find, therefore, is that the form of the conductance curve is determined by the dielectric constant of the solvent. The relation between the conductance and the dielectric constant is therefore shown most readily by bringing out the relation between the constants of the conductance function and the dielectric constant. In the following table are given values of the

[15] Thomson, *Phil. Mag.* [5] *36*, 320 (1893).
[16] Nernst, *Ztschr. f. phys. Chem.* *13*, 531 (1894).

dielectric constant and the constants *m*, *D*, and *K* for electrolytes in different solvents. So far as possible, typical electrolytes have been chosen, since, as we have seen, the constants are in general a function of the electrolyte. We have seen, however, that the typical electrolytes behave similarly in a given solvent, so that a rough comparison may be made between the dielectric constant and the various constants which determine the form of the conductance function. Those values of *D* which appear in parentheses have been calculated from the values of *P*, assuming that the value of Λ_0 is proportional to the fluidity of the solvent. This relation is not strictly true, particularly in the case of the inorganic solvents. However, it unquestionably gives the order of magnitude of this constant.

TABLE XXXII.

CONSTANTS OF EQUATION 11 AND DIELECTRIC CONSTANTS FOR VARIOUS SOLVENTS.

Solvent	Solute	Dielectric constant	*m*	*D*	$K\times10^4$
Hydriodic acid	$(C_2H_5)_3N.HCl$	2.9	1.58	(0.58)	....
Amylamine	$AgNO_3$	4.5	1.67	....	....
Propionic acid	LiBr	5.5	1.74	(0.30)	....
Methylaniline	$C_6H_5N.HBr$	5.9	1.64	....	....
Ethylamine	$AgNO_3$	6.2	1.45	(0.22)	2.4×10^{-4}
Ethylamine	NH_4Cl	6.2	1.57	....	....
Hydrobromic acid	$(C_2H_5)_3N.HCl$	6.3	1.51	(0.54)	....
Aniline	$AgNO_3$	7.5	1.42	(0.44)	....
Aniline	NH_4I	7.5	1.44	(0.51)	....
Hydrochloric acid	$(C_2H_5)_3N.HCl$	9.5	1.42	(0.39)	....
Acetic acid	LiBr	9.7	1.43	(0.30)	....
Phenol	$(CH_3)_4NI$	9.7	1.28	0.69	2.8
Hydrogen sulfide	$(C_2H_5)_3N.HCl$	10.0	1.58	(0.30)	....
Methylamine	$AgNO_3$	10.0	1.22	0.30	0.80
Ethylenechloride	$(C_3H_7)_4NI$	10.5	..	....	1.45
Pyridine	NaI	12.4	..	....	13.0
Pyridine	KI	12.4	..	....	5.2
Acetoaceticester	NaSCN	15.7	..	....	9.5
Isoamylalcohol	NaI	15.9	1.2	0.403	5.85
Isoamylalcohol	LiI	15.9	..	....	7.3
Acetophenone	NaI	16.4	..	....	34.0
Sulfur dioxide	KI	16.5	1.14	0.40	8.5
Methylethylketone	NaI	18.4	..	....	23.0
Isobutylalcohol	NaI	18.9	..	....	12.0
Acetone	NaI	21.8	..	....	39.0
Ammonia	NaI	22.0	0.83	0.43	28.0
Ammonia	$AgNO_3$	22.0	0.83	0.36	28.0
Epichlorhydrin	$(C_2H_5)_4NI$	22.6	..	....	48.5
Propylalcohol	NaI	23.0	0.75	0.208	38.3
Benzonitrile	NaI	26.0	..	....	55.0

The solvents are arranged in the order of their dielectric constants. It will be observed, in the first place, that the constant *D* is in all cases of the same order, varying between 0.2 and 0.69 with a mean value in the

neighborhood of 0.4. This constant, therefore, is a characteristic property of the electrolyte upon which the solvent has only a secondary influence. In this connection, it is to be borne in mind that various complexes may be formed between an electrolyte and its solvent, upon the nature of which complexes the constant D may depend. We should therefore expect a certain amount of variation in the value of the constant D for a given electrolyte in different solvents. Probably the change in the value of D would be found to be much smaller in case the dielectric constant were altered, not by a change of the solvent medium, but by a change of the temperature. The constant m is seen to decrease as the dielectric constant increases. Since this constant is a property of the electrolyte, as well as of the solvent, it follows that an exact comparison cannot be made. However, it is clear that, for solvents of very low dielectric constant, the value of m approaches 2, whereas for solvents of very high dielectric constant the value of m is less than unity. In the case of water m appears to have a value in the neighborhood of 0.5. The change in the value of m as a function of the dielectric constant is well illustrated in the case of silver nitrate dissolved in the amines. For amylamine, ethylamine, aniline, methylamine, and ammonia the dielectric constants are respectively 4.5, 6.2, 7.5, 10 and 22, and the values of m are 1.67, 1.45, 1.42, 1.22 and 0.83. It is seen that throughout this series of solvents, which are similar in their constitution, the value of the constant m for silver nitrate decreases with increasing values of the dielectric constant.

The mass-action constant K decreases very rapidly as the dielectric constant decreases. While there are numerous transpositions in the order of the constants, which is to be expected, since this constant is a function of the constitution of the salt as well as that of the solvent, nevertheless, in a general way, there can be no question but that the mass-action constant K decreases as the dielectric constant decreases. The variation is much more regular when solutions in solvents of the same type are compared. So, in the case of solutions of silver nitrate in ammonia and its derivatives, the constants are as follows: ethylamine, 2.44×10^{-8}; methylamine, 0.8×10^{-4}; ammonia, 28×10^{-4}. When the dielectric constant falls below a value of approximately 10, the mass-action constant for the typical salts has reached a value in the neighborhood of 1×10^{-4} and thereafter it falls off very rapidly with decreasing values of the dielectric constant. No accurate data being available in dilute solutions of solvents having a dielectric constant less than 10, it is impossible to proceed further with the comparison. Assuming, however, that the conductance function holds, it is possible to calculate the values

of the constant K if sufficiently accurate data are available at intermediate concentrations. The value of K for solutions in ethylamine was obtained in this way. The extremely low value of the constant will be noted.

Having shown the relation between the constants of the conductance function and the dielectric constant, it will be unnecessary to give a detailed list of various solvents which have been found to yield electrolytic solutions. The general form of the conductance curve may at once be inferred from the value of the dielectric constant. Many salts are not, as a rule, soluble in solvents of low dielectric constant. Nevertheless, certain typical salts form solutions with many solvents of very low dielectric constant, as for example silver nitrate, which dissolves in amyl amine, which has a dielectric constant of only 4.5. Such behavior, however, is exceptional and is probably to be ascribed to the formation of soluble complexes between the salt and the solvent. Various salts of organic bases, however, as has already been stated, are soluble in solvents of very low dielectric constant.

The question has been raised as to the influence of the electrolyte on the dielectric constant of the medium in which it is dissolved. Walden,[17] who has measured the dielectric constants of some non-aqueous solutions, concluded that the dielectric constant is greatly increased due to the addition of an electrolyte and has suggested that the observed deviations of strong electrolytes from the simple mass-action law are due to this factor. More recently, however, Lattey [18] has subjected the methods of measuring the dielectric constant of electrolytes to careful examination and has himself carried out measurements on numerous aqueous solutions. He finds that the dielectric constant of electrolytic solutions is considerably lower than that of the pure solvent. For example, for a solution of potassium chloride in water of concentration 0.00755 normal he obtained the value 66.25 as against 81.45 for pure water. The dielectric constant diminishes approximately as a linear function of the concentration and the effect for different electrolytes is of the same order of magnitude. Further investigations in this direction are much needed.

The precise form of the functional relation between the dielectric constant of the solvent and the ionization of the dissolved electrolyte is unknown. Walden [19] has suggested an empirical relation according to which the ionization of a typical electrolyte is the same in different solvents when the product of the dielectric constant and the cube root

[17] Walden, *Bull. Acad. St. Petersb.* *6*, 305 and 1055 (1912); *J. Am. Chem. Soc.* *35*, 1649 (1913).
[18] Lattey, *Phil. Mag.* *41*, 829 (1921).
[19] Walden, *Ztschr. f. phys. Chem.* *54*, 228 (1905).

of the dilution have the same value. More recently, a number of writers have proposed theories of electrolytic solutions which lead to Walden's relation as a consequence. Walden has made an extensive study of available data [20] from which he draws the conclusion that his relation holds practically without exception. The theories in question will be discussed in another chapter. We shall here consider Walden's relation from an experimental point of view only.

In mathematical terms, we have:

if

(37) $$\gamma_1 = \gamma_2 = \gamma_3 =, \text{etc.}$$

then

(38) $$\varepsilon_1 V_1^{\frac{1}{3}} = \varepsilon_2 V_2^{\frac{1}{3}} = \varepsilon_3 V_3^{\frac{1}{3}} = , \text{etc.}$$

where ε is the dielectric constant of the medium and V is the dilution of the solution of a given electrolyte, whose ionization fulfills the condition 37. Walden has tested the relation by comparing the values of $\varepsilon V^{\frac{1}{3}}$ for solutions of typical electrolytes in different solvents and believes to have shown that this quantity is a constant within the limits of experimental error and minor variations due, perhaps, to differences in the condition of the electrolyte in different media.

It is clear, from Equation 38, that a small variation in the value of the product $\varepsilon V^{\frac{1}{3}}$ will have as a result a large variation in the resulting conductance curve, since the dilution enters as the cube root. Actually the variations of the constants are quite large. For example, at an ionization of 82%, the product $\varepsilon V^{\frac{1}{3}}$ in water has a value of 156, in ammonia 286, in isobutylalcohol 333, and in ethylene chloride 315. The constancy of the values which Walden has found is in part due to the use of unreliable conductance data and in part to the use of Λ_0 values which are unquestionably in error.

It is obvious, according to Equation 38, that, if the ionization curve is fixed for a typical electrolyte in one solvent, it is fixed for typical electrolytes in all other solvents. For we have, considering solutions of a given electrolyte in two different solvents,

$$\varepsilon_1 V_1^{\frac{1}{3}} = \varepsilon_2 V_2^{\frac{1}{3}},$$

(39) $$\text{or} \quad V_2 = \left(\frac{\varepsilon_1}{\varepsilon_2}\right)^3 V_1.$$

If V_1 is the dilution in the first medium, at which the ionization of the electrolyte is γ, then V_2, as determined by Equation 39, is the dilution in

[20] Walden, *Ztschr. f. phys. Chem.* 94, 263 (1920).

the second medium at which the electrolyte will have the same ionization.

In the following table are given values of V calculated according to Equation 39, at which the ionization of typical electrolytes is 70% and 95% in different solvents, based upon an aqueous solution of sodium chloride as reference medium. Under $V_{obs.}$ are given the observed dilutions at which solutions in the various solvents have the ionization in question.

TABLE XXXIII.

OBSERVED AND CALCULATED VALUES OF THE DILUTION V AT WHICH TYPICAL ELECTROLYTES IN VARIOUS SOLVENTS HAVE THE SAME IONIZATION.

Solvent	Water	Ethyl Alcohol	Epichlorhydrin	Acetophenone	Pyridine	Ammonia	Isobutyl-alcohol	Ethylene chloride
Dielectric constant	81.7	25.6	22.6	18.2	13.0	22.0	18.9	10.5
Λ_0	108.9	39.42	62.1	33.3	57.0	339.0	12.8	66.7
Temp.	18°	25°	25°	25°	18°	−33.5°	25°	25°
Ioniz. = 70%:								
$V_{obs.}$	1.207	125.9	159.1	320.5	861.0	794.5	1348.0	11290.0
$V_{calc.}$	1.207	39.2	56.8	109.0	299.0	61.7	97.5	569.0
Ioniz. = 95%:								
$V_{obs.}$	181.0	3590.0	3350.0	5970.0	25110.0	11910.0	14620.0	....
$V_{calc.}$	181.0	5880.0	8530.0	16300.0	44900.0	9260.0	14600.0	....

The electrolyte employed for comparison is sodium iodide, except in the case of water, epichlorhydrin, ethylene chloride and ammonia, in which the electrolytes were sodium chloride, tetraethylammonium iodide, tetrapropylammonium iodide and potassium nitrate, respectively. So far as solutions in water are concerned, the ionization values correspond very closely for different binary electrolytes, so that it is a matter of indifference whether one or another typical binary electrolyte is employed as reference electrolyte. At the higher concentrations, it is true, the value of γ is somewhat lower for sodium chloride than for potassium chloride. However, this does not affect the comparisons appreciably; if anything, the comparison is somewhat more favorable with sodium chloride than with potassium chloride as reference electrolyte.

If Equation 38 were applicable, the calculated values of V should everywhere correspond with the observed values. At an ionization of 70% the calculated values of V are in all instances too small. The discrepancy is greatest in the case of ethylene chloride at 70% ionization, which, according to calculation, should be 569 liters, whereas the measured dilution is 11,290. In general, the lower the dielectric constant of

the medium, the greater the discrepancy between the observed and calculated values, although there are some marked exceptions. Furthermore, the order of the deviations varies as the ionization of the electrolyte varies. This is particularly noticeable in the case of ammonia and isobutyl alcohol, where the observed and calculated values very nearly agree at 95% ionization, but diverge largely at an ionization of 70%. On the other hand, in other cases, the deviation changes sign. For example, at 70% ionization the observed value for ethyl alcohol is 125.9 and the calculated value 39.2, whereas at 95% ionization the observed value is smaller, being 3590, and the calculated value 5880.

That Walden's relation cannot hold generally may most readily be shown by graphical means. If we take logarithms of both sides of Equation 39, we have:

$$\log V_2 - \log V_1 = 3 \log \frac{\varepsilon_1}{\varepsilon_2}.$$

If the values of γ for an electrolyte in different solvents are plotted against values of $\log V$, then obviously for any given value of γ the abscissas on the curves will differ by $3 \log \frac{\varepsilon_1}{\varepsilon_2}$. In other words, the curve *for an electrolyte in any one solvent may be derived from that in any* other solvent by merely displacing the curve along the axis of $\log V$ by an amount equal to $3 \log \frac{\varepsilon_1}{\varepsilon_2}$. An inspection of Figure 3, where values of γ for different solvents are plotted as functions of $\log V$, shows at once that this condition is not fulfilled, for, if the curve for water were displaced parallel to itself, it would not coincide with the curves for solutions of typical electrolytes in other solvents, such as ethyl alcohol, ammonia and ethylene chloride. Indeed, in order to test the applicability of Walden's relation it is not even necessary to know the value of Λ_0, since it follows readily from Equation 39 and from the equation $\gamma = \frac{\Lambda}{\Lambda_0}$ that if the conductances themselves are plotted as functions of $\log V$, it must be possible to derive the curve for an electrolyte in any one solvent from that in any other solvent by displacing the curve parallel to itself in some direction, this direction being determined by the values of Λ_0 and of the dielectric constant ε. Those familiar with the properties of electrolytic solutions will at once recognize that this condition is not fulfilled.

Actually, it is not to be expected that any simple relation will exist between the ionization γ and the dielectric constant of the solvent, for,

change in the speed of the carriers. It should be stated, however, in this connection, that no theory has thus far been proposed which adequately accounts for the change in the carrying capacity of the ions as a function of the concentration, particularly in solvents of low dielectric constant. Any such theory must not only account for an initial diminution in the speed of the ions, but it must also account, in many cases, for a subsequent increase in the speed with increasing concentration. In fact, such a theory must account for the various forms of the conductance curves in different solvents and for the change in the form of the curves as the condition of the solvent is altered. Incidentally, it is to be noted that the order of the changes in the speed of the ions on this assumption is very great. It is true that, in aqueous solutions, the speed does not vary greatly from the most dilute solutions up to normal concentration, but in solutions in solvents of low dielectric constant it is not only necessary to account for a decrease in speed but in many cases for an increase in speed which, over a limited range of concentration, is, at times, as great as a thousandfold. It seems very difficult to account for a change of speed of this magnitude on the basis of our present knowledge of the properties of the carriers in different media. In this connection it should be borne in mind that, superimposed on these hypothetical changes in the speed of the ions, there is a change due to the viscosity of the solution which effect appears in every respect to be normal in character. Furthermore, solutions of weak electrolytes, both in water and non-aqueous solvents, conform to the mass-action law up to fairly high concentrations. If the speed of the ions changes with the concentration, then such a simple relation is not to be expected.

A third hypothesis has been proposed, namely: that the ionization reaction differs from that which is commonly assumed. Certain writers have made the assumption that, in non-aqueous solutions, the electrolyte is associated, the association changing with concentration, and that only the associated molecules are capable of ionization. They assume, for example, in the simplest case, that the following reactions take place:

$$MX + MX = (MX)_2$$
$$(MX)_2 = M_2X^+ + X^-$$

As the concentration increases, the amount of the polymer increases and this increase might be sufficient to provide for an actual increase in the number of ions present. If this hypothesis is correct, the current in such solutions is carried chiefly by complex ions and consequently transference numbers in such solutions should be abnormal. Reliable transference numbers in solvents of low dielectric constant are not available,

but from the data for solvents of somewhat higher dielectric constant it may be inferred that the transference numbers are approximately normal. Furthermore, since it appears that the deviations from the mass-action law in aqueous solutions are of the same character as in non-aqueous solutions, it follows that similar intermediate ions would have to be assumed to be present in solutions of the strong binary electrolytes in water. If such were the case, not only should the transference numbers be abnormal, but they should vary as a function of the concentration. Now, while it is true that many transference numbers do vary with the concentration, a considerable variation takes place only at relatively high concentrations, and only at such concentrations where the viscosity of the solution has increased sufficiently to materially affect the motion of the ions through the solution. It would seem that transference measurements should yield data corroborating this last hypothesis if it were correct. So far as available data are concerned, the hypothesis is not substantiated.

4. *The Form of the Conductance Curve in Dilute Aqueous Solutions.* The applicability of the conductance function to aqueous solutions is uncertain. That the Storch equation holds approximately for aqueous solutions at higher concentrations has long been known. In the case of Equation 11 this would yield for m values of approximately 0.5, and for D values in the neighborhood of 2. With such large values of the constant D and small values of the constant m, it becomes very difficult to determine the value of the constant K. At concentrations sufficiently low, so that the effect of the D term might be neglected, the ionization is so nearly complete that it becomes practically impossible to demonstrate whether or not the mass-action law is approached as a limiting form. Kraus and Bray have shown that Equation 11 may be applied with considerable exactitude to solutions in water up to 10^{-3} normal, provided a value of Λ_0 is chosen which is lower than the experimentally determined values of the equivalent conductance at very low concentrations. More recently, Washburn and Weiland[21] have concluded from their very accurate conductance measurements on KCl up to 2×10^{-5} normal that the mass-action law is actually approached as a limit. Their results, however, do not appear to be conclusive, since, in extrapolating for the value of Λ_0, they assume the mass-action law to hold.[22] If the mass-action constant is calculated with a value of Λ_0 based on the assumption that the mass-action law holds, then the results must necessarily conform to the assumption made. The curve obtained

[21] Washburn and Weiland, *J. Am. Chem. Soc.* *40*, 106 (1918).
[22] Kraus, *J. Am. Chem. Soc.* *42*, 1 (1920).

is shown in Figure 14, in which values of the mass-action function K' are plotted against those of the concentration. The form of this function is entirely different from that which has been found to hold in solutions in non-aqueous solvents and it is obvious, moreover, that the function is a comparatively complex one. At higher concentrations, and practically down to 1.5×10^{-4} normal, the K', C-curve is everywhere concave toward the axis of concentrations. At this low concentration, however, the curve changes its form, and approaches a value asymptotic to a line parallel to the axis of concentrations. In order to establish the mass-action law as a consequence of experimental observations it must be

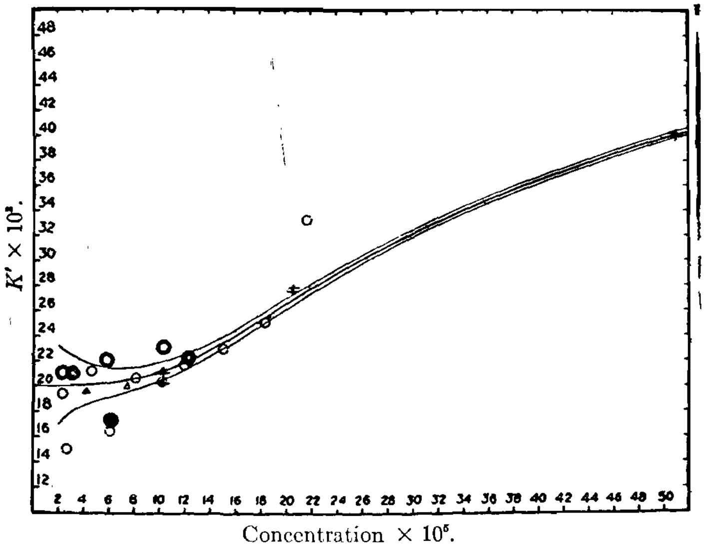

FIG. 14. Showing Variation of K' with Concentration for Aqueous Solutions of KCl at 18° According to Washburn.

shown that, over a measurable concentration interval, points on the curve necessarily lie upon a horizontal straight line. As this has not been done, it is evident that Washburn's conclusions remain in doubt.

The manner in which the curve for the mass-action function approaches the axis depends upon the value of the constant m in the general equation. For values of m greater than unity, the curve approaches the axis asymptotic to a line parallel to the axis of concentrations; while for values of m less than unity, it approaches the axis asymptotic to the axis of K'. In the case of water, therefore, for which the value of m appears to be less than unity, we should expect that the K' curve would be everywhere concave toward the axis of concentrations.

The conductance of potassium chloride solutions between the concentrations of 10^{-2} and 2×10^{-5} normal may be represented well within the limits of experimental error, by means of the Equation 11 [23] in which the constants have the value: $m = 0.52$, $D = 1.703$, $\Lambda_0 = 129.9$, and $K = 10 \times 10^{-4}$. Washburn's value for K is 200×10^{-4}. Actually, this represents an upper probable limit for the value of the constant K. The value 10×10^{-4} would appear to be too small. Salts in the alcohols have values of the mass-action constant considerably greater than this. Since, in general, the value of the mass-action constant increases with the dielectric constant, we should expect that the value of this constant in the case of aqueous solutions would be greater than in the alcohols. It should be noted, however, that the experimental results might still be represented within the limits of experimental error if a value considerably greater than 10×10^{-4} were assumed for the mass-action constant. It is possible, therefore, that the salts in water may have a value of the mass-action constant as high as 100×10^{-4}. On the other hand, so far as the actual data are concerned, it cannot be definitely demonstrated that the mass-action law is approached as a limiting form in aqueous solutions of strong electrolytes. Even the value of 200×10^{-4} for potassium chloride appears to be distinctly lower than the value of the constants for certain much weaker electrolytes in aqueous solution, as, for example, acids of intermediate strength.

In the case of the strong acids and bases, sufficient data are not available to determine the order of magnitude of the limit which the function K' approaches. If the data relating to hydrochloric acid are correct, the ionization of this acid in a 10^{-4} normal solution is as low as that of potassium chloride at the same concentration, assuming that the value of Λ_0 for hydrochloric acid is 380.0. Actually this value of Λ_0 is somewhat too low and the value 382.0 is probably more nearly correct. It would appear, therefore, that the strong acids may approach a value of the mass-action constant as low or lower than that of the salts; or, in other words, values lower than 200×10^{-4}. No data are available from which the ionization of the strong bases may be calculated at low concentrations.

The limiting values which the ionization constants of the strong acids and bases approach at low concentrations is of considerable practical importance, since the hydrolysis of salts depends upon the relative values of these constants and that of water. If the values which the mass-action constants of the bases and acids approach at low concentrations are sufficiently small, then the salts of these acids and bases will be

[23] Kraus, *loc. cit.*

hydrolyzed to an appreciable extent at very low concentrations. In case the limits approached differ for the acids and the bases, the measurement of the conductance of very dilute salt solutions will be affected by hydrolysis. It appears not impossible that the bases may approach values of the mass-action constant lower than those of the acids. In liquid ammonia solutions the ionization constants of the bases are much lower than those of the acids. We might, therefore, expect that at concentrations approaching 10^{-5} normal the conductivity of the salt might be appreciably affected by hydrolysis. This is almost certainly the case with silver nitrate. The ionization constant of this base is approximately 2.5×10^{-4} at 25°. This value is based on the solubility of a saturated solution of silver oxide in water whose ionization has been determined to be approximately 0.64. At 10^{-3} normal the conductance of the silver nitrate solution would be affected to the extent of 0.7 per cent due to hydrolysis. Until more accurate data are available on the ionization of the strong acids and bases at low concentrations, the interpretation of conductance measurements with salts at low concentrations remains in doubt.

5. *Solutions of Formates in Formic Acid.* It is evident, from the considerations of the foregoing sections, that, as the concentration of an electrolyte increases, the value of the function K' increases. In other words, as the concentration of the electrolyte increases, the conductance falls less rapidly than required by the simple mass-action relation. As we have seen, if the simple mass-action law holds, then a plot of the reciprocal of the equivalent conductance against the specific conductance, or the ion concentration, yields a linear relation between the experimentally determined points. Deviations from the mass-action law are then, obviously, such that at high concentrations the points diverge from a straight line toward the axis of specific conductances. In general, therefore, these curves are concave toward the axis of specific conductances. There are indeed a few cases in which the curves are convex toward the axis of specific conductances, or, in other words, in which the deviations from the mass-action relation are in the opposite direction. This has been found to be the case with aqueous solutions of certain weak organic acids whose viscosity is very high. Presumably this form of the curve is due to the rapidly increasing viscosity of the solution at higher concentration. The same form of curve has been found by Schlesinger and his associates for solutions of formates in formic acid.[24]

[24] Schlesinger and Calvert, *J. Am. Chem. Soc. 33,* 1924 (1911); Schlesinger and Martin, *J. Am. Chem. Soc. 36,* 1589 (1914); Schlesinger and Coleman, *J. Am. Chem. Soc. 38,* 271 (1916); Schlesinger and Mullinix, *J. Am. Chem. Soc. 41,* 72 (1919); Schlesinger and Reed, *J. Am. Chem. Soc. 41,* 1921 (1919); Schlesinger and Bunting, *J. Am. Chem. Soc. 41,* 1934 (1919).

According to Schlesinger, solutions of the formates in formic acid present an anomaly in that, while they are highly ionized, differing but little in this respect from aqueous solutions, the simple law of mass-action is obeyed up to concentrations as high as 0.3 normal. If this interpretation is correct, it will be necessary to revise all commonly accepted notions relative to the causes underlying the deviations from the simple mass-action law, since in these solutions we would have a case in which the law of mass-action is obeyed up to high concentration for solutions of strong electrolytes. We may, therefore, examine the results obtained

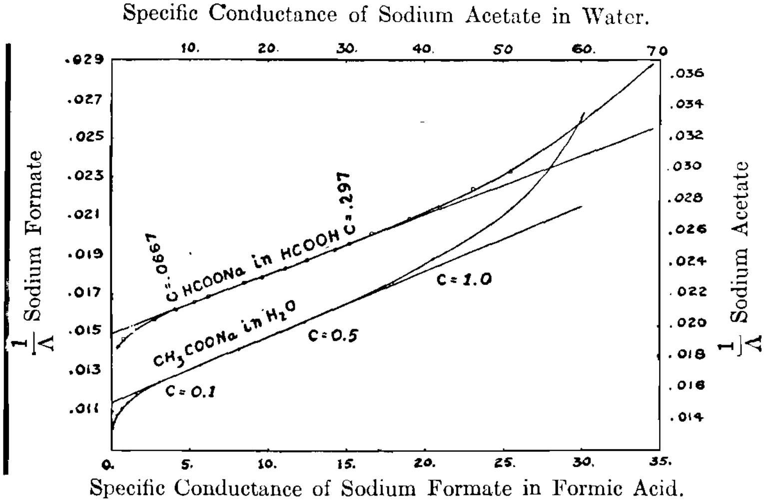

Fig. 15. Comparison of Conductance Curves in Formic Acid and in Water.

in formic acid with some care in order to determine whether or not solutions in this solvent may be brought into line with solutions in other solvents.

It is at once apparent that measurements with solutions in formic acid may lead to difficulties of interpretation, owing to the fact that the conductance of the pure solvent is very high. It is not possible to carry the measurements to very low concentrations; and if such measurements are carried out, the results will always be more or less in doubt. In Figure 15, the upper curve represents a plot of $1/\Lambda$ against the specific conductance for solutions of sodium formate in formic acid, according to Schlesinger. It will be observed that, between a concentration of $C = 0.0667$ and $C = 0.297$, the points lie upon a straight line within the limits of experimental error. At lower concentrations the curve deviates from a straight line, being concave toward the axis of

ion concentrations, while at higher concentrations it is convex toward this axis; in other words, the experimentally determined points lie upon a curve which has an inflection point somewhere between the concentrations given above, probably in the neighborhood of 0.1 normal. Schlesinger is inclined to attribute the deviation of the points in the more dilute solutions to the presence of impurities. So far as the conductance of the solvent is concerned, since sodium formate has an ion in common with formic acid, it is to be expected that the ionization of formic acid itself will be repressed by sodium formate, so that the conductance of the pure solvent itself will not enter. He believes, however, that there are present in the solvent impurities, as a result of which the measured conductance is higher than that due to the electrolyte. On the other hand, it is known that the salts of the fatty acids yield ions which move very slowly and whose solutions exhibit an extremely high viscosity. The form of the curve in the case of the formates in formic acid is similar to that of certain acids in water. Further light may be thrown upon this question by considering the conductance curves of salts of organic acids in water, whose solutions likewise exhibit a high viscosity. The lower curve in Figure 15 represents a plot of $1/\Lambda$ against the specific conductances for sodium acetate in water at 18°. An inspection of the figure shows at once that the curve for sodium acetate in water is in all respects similar to that of sodium formate in formic acid. Between the concentrations 0.1 and 0.5 normal, the points lie upon a straight line within the limits of experimental error. In the more dilute solutions, the experimentally determined points lie upon a curve concave toward the axis of concentrations and in the more concentrated solutions on a curve convex toward this axis. In the case of sodium formate in formic acid, the concentration interval over which the points lie upon a straight line is 0.0667 to 0.297, corresponding to a concentration ratio of 4.45, while in the case of sodium acetate in water the corresponding concentration interval is 0.1 normal to 0.5 normal, whose ratio is 5.0. If we hold that the law of mass-action applies to solutions of sodium formate in formic acid, we might equally well hold that this law applies to solutions of potassium acetate in water. Our knowledge of the behavior of aqueous solutions, however, is such that it is at once evident that the linear form of the curve between 0.1 and 0.5 normal is due to the fact that, owing to the high viscosity of the solutions at higher concentrations, the conductance as measured is smaller than it otherwise would be. On the other hand, in the more dilute solutions the form of the curve in the case of sodium acetate is entirely similar to that of other binary electrolytes in water. It is difficult, therefore, to escape the con-

clusion that in the case of solutions of the formates in formic acid, likewise, the approximately linear form of the curve over a limited concentration interval is due to the existence of an inflection point and that the causes underlying the course of the curve are the same as those in solutions of sodium acetate in water. It appears probable, therefore, that solutions of the formates in formic acid do not constitute an exception to the well-known behavior of strong electrolytes in solvents of high dielectric constant. From this point of view these solutions are normal in their behavior.

6. *The Behavior of Salts of Higher Type.* Up to this point, the electrolytes considered have been of the binary type. In the case of salts of higher type the interpretation of conductance measurements becomes much more difficult and uncertain, since it is possible, and even probable, that ionization may take place in several stages, as indeed it does in the case of weak acids and bases. For example, a salt of the type MX_2 may ionize according to the equations:

$$MX_2 = MX^+ + X^-$$
$$MX^+ = M^{++} + X^-$$
$$MX_2 = M^{++} + 2X^-.$$

If ionization takes place only according to the last equation, then the degree of ionization may be calculated from conductance measurements. But if ionization takes place according to the first two equations, then it is not possible to determine the number of carriers in the solution at a given concentration. In the case of weak dibasic acids, ionization often takes place according to the first two equations, the constants of the two reactions being such that one reaction is practically completed before the other reaction has begun. With salts this does not appear to be the case.

In any case, if the concentration is sufficiently low, we should expect that, ultimately, there would be present in the solution only the ions M^{++} and X^-. Since the ion M^{++} carries two charges, its carrying capacity will be approximately twice as great as that of an ion carrying only a single charge. The molecular conductance of such an electrolyte should therefore approach a value approximately twice that of a binary electrolyte, or its equivalent conductance should approach a value of the same order as that of binary electrolytes. An examination of the conductances given in Table III indicates that this is the case. The limiting value of the equivalent conductance for salts of different type is throughout of the same order, and we may conclude, therefore, that at low concen-

trations the carrying capacity of an electrolyte is determined by the number of charges associated with the ionic constituents.

In solutions of salts of the type of copper sulphate, reaction may take place according to the equation:

$$CuSO_4 = Cu^{++} + SO_4^{--}.$$

This reaction is a binary one, similar to that of the binary salts, but the molecular conductance of such a salt should be twice that of a binary salt. Such has been found to be the case.

This behavior of salts of higher type appears to be quite general and is not confined to aqueous solutions. In Table XXXIV are given conductance values for solutions of strontium and barium nitrates in ammonia. It will be observed that in both cases the limiting value of the molecular conductance is much higher than that of binary electrolytes and is, in fact, approximately twice that of these electrolytes. We may assume, therefore, that in these solutions we have ultimately a reaction corresponding to the type:

$$Sr(NO_3)_2 = Sr^{++} + 2NO_3^-.$$

It is apparent, however, that at a given concentration the number of carriers present in solutions of these electrolytes is much lower than it is in solutions of typical binary electrolytes. Owing to the low value of the ionization, the values of Λ_0 for electrolytes of this type have not been determined with any degree of certainty.

TABLE XXXIV.

CONDUCTANCE OF TERNARY SALTS IN NH_3 AT —33°.

$Sr(NO_3)_2$ [25]		$Ba(NO_3)_2$ [26]	
V	Λ_{mol}	V	Λ_{mol}
286.2	145.0	91.1	101.3
1283.0	207.0	1407.0	200.6
5441.0	275.8	14950.0	319.4
20360.0	359.3	58750.0	422.5
61660.0	449.0	116500.0	498.5
151100.0	514.2		

Similar results have been obtained with solutions of ternary electrolytes in various other solvents, such as acetone, pyridine, and the like. In many cases, however, the solubility of these salts is relatively low and their ionization at ordinary concentrations is often extremely small. They do not, therefore, lend themselves to a quantitative study of the

[25] Franklin and Kraus, *Am. Chem. J.* 23, 292 (1900).
[26] Franklin and Kraus, *J. Am. Chem. Soc.* 27, 200 (1905).

relation between the conductance and the concentration. In the case of aqueous solutions, however, sufficient data are available to make it possible to obtain a general notion as to the manner in which the conductance varies as a function of concentration. Assuming a reaction of the type

$$MX_2 = M^{++} + 2X^-,$$

and assuming the mass-action law to apply, we obtain the equation:

$$\frac{C^2\gamma^3}{1-\gamma} = K'.$$

In Table XXXV are given values of the function K' calculated according to the above equation at a series of concentrations for calcium chloride dissolved in water at 18°.

TABLE XXXV.

VALUES OF THE MASS-ACTION FUNCTION FOR $CaCl_2$ SOLUTION IN H_2O AT 18°.

C	10^{-3}	5×10^{-3}	2×10^{-2}	10^{-1}	5×10^{-1}
γ	.954	.910	.849	.764	.686
K	1.88×10^{-5}	1.7×10^{-4}	1.62×10^{-3}	1.88×10^{-2}	2.6×10^{-1}

It will be observed that the mass-action function for this salt increases very greatly with the concentration. On the whole, the increase is much more marked than it is for binary electrolytes. The value of the function, moreover, is much lower throughout than it is for solutions of binary electrolytes. At 5×10^{-1} normal the value of K' is only 0.26, which is approximately one-half that of potassium chloride, while at 10^{-3} normal the value is 1.88×10^{-5}. The mass-action function, therefore, falls off very rapidly as the concentration decreases. In the case of copper sulphate solutions we have the equation:

$$\frac{C\gamma^2}{1-\gamma} = K'.$$

Values of the mass-action function for this electrolyte at different concentrations are given in Table XXXVI. At higher concentrations the value of the function K' for this salt is smaller than that for calcium chloride, but the constant decreases much less rapidly as the concentration decreases and at lower concentration the value of the function is much greater than that of calcium chloride. On the whole, the function appears to undergo a smaller change with the concentration in the case of copper sulphate than in that of uni-univalent electrolytes. However, it

is to be borne in mind that the value of Λ_0 for this electrolyte is much less certain than that for the uni-univalent salts.

TABLE XXXVI.

VALUE OF THE MASS-ACTION FUNCTION FOR $CuSO_4$ IN H_2O AT 18°.

C	10^{-3}	5×10^{-3}	2×10^{-2}	10^{-1}	1.0
$\gamma\%$....	86.2	70.9	55.0	39.6	30.9
K	5.4×10^{-3}	8.6×10^{-3}	1.34×10^{-2}	2.6×10^{-2}	1.38×10^{-1}

As the salts become more complex, the value of the mass-action function becomes smaller and decreases more rapidly as the concentration decreases. For potassium ferrocyanide, assuming the reaction equation:

$$K_4FeCN_6 = 4K^+ + FeCN_6^{----},$$

the mass-action function has the form:

$$\frac{(C\gamma)^4}{C(1-\gamma)} = K'.$$

Values of the function at different concentrations are given in Table XXXVII for this salt, as well as for lanthanum sulphate. The constant for the ferrocyanide is throughout small and at low concentrations approaches values of an entirely different order of magnitude from that at the higher concentrations. In the case of lanthanum sulphate, the change in the constant is even more pronounced, as may be seen from an inspection of the table.

TABLE XXXVII.

VALUES OF THE MASS-ACTION FUNCTION OF AQUEOUS SALT SOLUTIONS.

K_4FeCN_6

C	2×10^{-3}	1.25×10^{-2}	5.0×10^{-2}	1.0×10^{-1}	3.0×10^{-1}	4.0×10^{-1}
$\gamma\%$	85.8	71.0	68.7	53.2	48.8	45.3
K	$.52\times10^{-10}$	1.5×10^{-8}	1.03×10^{-6}	0.920×10^{-5}	4.33×10^{-4}	0.925×10^{-3}

$La_2(SO_4)_3$

C..........	2×10^{-3}	10^{-2}	5×10^{-2}
$\gamma\%$	51.4	33.9	26.2
K	1.28×10^{-12}	0.67×10^{-10}	1.03×10^{-8}

It is obvious that, in solutions of electrolytes of higher type, the mass-action function varies the more the higher the type of the salt. The value which the function appears to approach at very low concen-

trations becomes extremely small and it is uncertain whether or not the function approaches a limiting value other than zero. The interpretation of the results, moreover, is rendered uncertain owing to the possible formation of intermediate ions. It might be expected, however, that, in the limit, the intermediate ions will disappear and the function will correspond to the usual mass-action function.

Although the curves become quite complex for salts of higher type, it appears, nevertheless, that the conductance curves at higher concentrations have the same general form as for salts of simpler type, and that they vary in a similar manner as the nature of the solvent varies. In the following tables are given values for the conductances of $Cu(NO_3)_2$ and $K_2Hg(CN)_4$ in ammonia.[27]

TABLE XXXVIII.

CONDUCTANCE OF TERNARY SALTS IN NH_3 AT —33°.

$Cu(NO_3)_2$		$K_2Hg(CN)_4$	
V	Λ	V	Λ
1.5	98.3	2.0	198.8
4.9	82.9	5.0	182.7
9.9	78.2	19.6	159.8
19.9	80.9	49.8	169.2
323.0	151.8	590.0	298.9
1300.0	213.7	4545.0	493.1
11190.0	417.0		
22450.0	498.0		

It will be observed that, in both cases, the conductance passes through a minimum value at concentrations in the neighborhood of 0.1 normal. In other words, an increase in the conductance with the concentration at the higher concentrations is not confined to binary electrolytes, but is more or less typical of all electrolytes. It appears, therefore, that the general form of the conductance function is the same for electrolytes of different types. What the precise form of the equation may be, however, has not been determined, since the Λ_0 values are unknown and the problem is complicated owing to the possible formation of intermediate ions.

[27] Franklin, *Ztschr. f. phys. Chem.* *69*, 272 (1909).

Chapter V.

The Conductance of Solutions as a Function of Their Viscosities.

1. *Relation Between the Limiting Conductance Λ_0 and the Viscosity of the Solvent.* One of the factors upon which the conductance of a solution depends is the viscosity of the solution itself. If conductance is due to the motion of charged particles through a medium, then the speed of the particles will obviously depend upon the resistance which the particles experience in their motion; that is, upon the viscosity of the medium. Unless the solutions are concentrated, their viscosities will not differ materially from that of the pure solvent. We should therefore expect that the viscosity of the pure solvent would determine the motion of particles under otherwise given conditions. We shall accordingly examine the relation between the conductance and the viscosity of solutions in different solvents. In very dilute solutions we may expect that the motion of a given particle will be practically independent of that of other particles of the electrolyte which may be present in the solution. In the limit, therefore, the Λ_0 values will be determined by the nature of the moving particles and by that of the solvent medium in which they move. In Table XXXIX [1] are given fluidity and Λ_0 values for solutions in a number of solvents, together with the values of the ratio Λ_0/F.

TABLE XXXIX.

FLUIDITY AND Λ_0 VALUES FOR ELECTROLYTES IN DIFFERENT SOLVENTS.

Solvent	Temp.	$F = 1/\varphi$	Λ_0	Λ_0/F	Electrolyte
Water	18°	93.9	111.0	1.173	NaI
Ammonia	—33°	391.0	301.2	0.770	"
Sulphur dioxide	—10°	233.4	199.0	0.854	KI
Benzonitrile	25°	80.0	49.0	0.613	NaI
Epichlorohydrin	25°	97.1	62.1	0.649	$(C_2H_5)_4NI$
Propylalcohol	18°	42.5	20.6	0.486	NaI
Acetone	18°	304.0	167.0	0.550	"
Methylethylketone	25°	249.0	139.0	0.560	"
Pyridine	18°	101.0	61.0	0.603	"
Isobutylalcohol	25°	29.6	13.7	0.463	"
Acetoaceticester	18°	59.4	30.7	0.517	"
Isoamylalcohol	25°	27.2	9.2	0.338	"
Ethylenechloride	25°	127.9	66.7	0.522	$(C_3H_7)_4NI$

[1] These values are taken from Kraus and Bray (*loc. cit.*, p. 1383), excepting those for water and the viscosity data for sulphur dioxide for which see Fitzgerald, *J. Phys. Chem.* *16*, 621 (1912).

So far as possible the same electrolyte, namely sodium iodide, has been employed for the purpose of comparison. In a few cases, however, results with this electrolyte are not available and the data for other iodides are therefore given. If the speed of the ions is solely a function of the viscosity of the solvent and is independent of the nature of the electrolyte, the nature of the solute will have no influence on the ratio of conductance to fluidity. As we shall see below, this is not the case.[2] On examining the table it will be seen that the limiting value of the conductance is roughly proportional to the fluidity of the solvent. The ratios Λ_0/F given in the last column vary between 0.338 for isoamyl-alcohol and 1.173 for water. These are, however, extreme values, and in the greater number of cases the ratio has a value of approximately 0.6. The three inorganic solvents, water, ammonia and sulphur dioxide, show exceptionally high values of the conductance-fluidity ratio. The higher alcohols have exceptionally low values, the value in general being the smaller the more complex the alcohol. In comparing the Λ_0 values of the salts in different solvents, we are comparing the sum of the conductances of the two ions. We may therefore expect to obtain a more nearly comparable result if we compare the conductances, not of the electrolytes, but of the individual ions of the electrolytes. The ratios of the ionic conductances for the different ions in ammonia and in water have been given in Table V. An examination of that table shows that the ratios of the ionic conductances vary all the way from 2.03 to 3.36, while the ratio of the fluidities of the two solvents is 4.15. It follows, therefore, that the ratio of the Λ_0 values for a given electrolyte in different solvents cannot be a constant, since the ratios of the ion conductances vary for different ions.

If a comparison is to be made between the conductance and the fluidity of electrolytes in different solvents, it might be expected that more nearly comparable results would be obtained if the more slowly moving ions were chosen for the purpose of comparison. For example, in water at 18°, the ratio of the conductance of the acetate ion to the fluidity of water is 0.367,[3] while in ammonia the ratio of the conductance of the CH_3CONH^- ion to the fluidity of ammonia at its boiling point is 0.330.

Apparently, therefore, the ratio of the ionic conductance to the fluidity of the solvent approaches a constant limiting value somewhere

[2] Walden [*Ztschr. f. phys. Chem.* 78, 257 (1912)] believes to have shown that, with a few exceptions, the ratio Λ_0/F is constant. In this he has been misled as a result of employing Λ_0 values obtained by extrapolating with the cube root formula of Kohlrausch which is not applicable.

[3] Based on the value 34.6 for the conductance of the acetate ion. Johnston, *J. Am. Chem. Soc.* *31*, 1010 (1909).

in the neighborhood of 0.3 as the ions become more complex; that is, as the speed of the ions decreases. It follows that, in the case of very slowly moving ions, the speed is inversely proportional to the viscosity of the medium, more or less independent of the nature of the solvent itself. It is interesting to compare the speed of ions due to radiations with the speed of ordinary ions in different solvents. In Table XL[4] are compared the speeds of the acetate ion in water, the lithium ion in ammonia, and the positive and negative ions in hexane. In the last column are given the values of the ratio of the speed of the ions to the fluidity in arbitrary units.

TABLE XL.

Comparison of Ionic Speeds in Different Solvents.

Solvent	Ion	Speed of ion $S \times 10^4$	F	S/F
Water	Acetate	3.58	95.35	3.76
Ammonia	Lithium	11.60	390.8	2.97
Hexane	Positive	6.03	312.0	1.98
Hexane	Negative	4.17	312.0	1.34

It will be observed that both positive and negative ions in hexane move decidedly slower than even the slowest moving ion in ammonia or in water, taking into account the relative viscosities of the solvent media. Apparently, in solvents of very low dielectric constant, the speed of the ions relative to the fluidity of the solvent is smaller than it is in solvents of higher dielectric constant. It may be inferred, therefore, that the positive and negative carriers in hexane are associated with a considerable number of the solvent molecules, as a result of which their speed is relatively low with respect to that of the ordinary ions in water and ammonia.

2. *Change of Conductance as Result of Viscosity Change Due to the Electrolyte Itself.* At higher concentrations the viscosity is a function of the concentration of the solution, and, in most cases, increases with it. In aqueous solutions there are, however, many cases in which the viscosity decreases at higher concentrations, or rather, in which the viscosity passes through a minimum, beyond which it again increases as the concentration increases. The viscosity effect of the electrolyte, therefore, is a property depending on the electrolyte as well as on the solvent. Solutions which exhibit a negative viscosity change with the concentration, that is, whose viscosity decreases with increasing concentration, are

[4] Kraus, *J. Am. Chem. Soc. 36*, 35 (1914).

also found in glycerine. In general, however, the negative viscosity effect appears only in the case of solutions in solvents having high dielectric constants. As a rule, only those salts which show relatively a slight tendency to form stable hydrates exhibit a negative viscosity effect in solution. In Table XLI are given examples of the relative viscosities of solutions in ammonia,[5] water, and methylamine[5] at a number of concentrations.

TABLE XLI.

COMPARISON OF THE VISCOSITY CHANGE DUE TO ELECTROLYTES IN DIFFERENT SOLVENTS.

Solvent	Solute	Relative Viscosity at Concentration: 0.5	1.0	2.5
Water	LiCl	1.05	1.10	1.42
Ammonia	KI	1.16	1.38	2.38
Methylamine	$AgNO_3$	1.40	1.96	6.38

It will be observed that in a 0.5 normal solution the viscosity increase for potassium iodide in ammonia is approximately three times that of lithium chloride dissolved in water, while the viscosity change for silver nitrate in methylamine at the same concentration is approximately three times that of potassium iodide in ammonia. Approximately the same ratio of increase holds at somewhat higher concentrations. In this connection it should be noted that the viscosity effect in the case of lithium chloride is relatively very great compared with that of other salts in water. In the case of potassium iodide the viscosity effect is actually negative in water. We see, therefore, that the lower the dielectric constant of the solvent, the greater is the increase in viscosity due to the added electrolyte. The dielectric constants are approximately 80, 22 and 10 for water, ammonia, and methylamine respectively. There are no data available relative to the viscosity of solutions in the higher amines, but qualitative data indicate that the viscosity effect increases very greatly with increasing complexity of the solvent, or, rather, with decreasing dielectric constant of the solvent. It is evident that there is a relation between the magnitude of the viscosity effect due to an electrolyte and the dielectric constant of the solvent in which this electrolyte is dissolved.

In Figure 16 are shown curves[6] representing the relation between the viscosity and the concentration of aqueous solutions of

[5] Fitzgerald, *loc. cit.*
[6] Sprung, *Pogg. Ann. d. Phys.* 159, *1* (1876).

potassium iodide at 0°, 30°, and 60° and sodium chloride at 10°, 30°, and 60°. It will be observed that the viscosity in the case of potassium iodide at 0° passes through a minimum in the neighborhood of 2½ normal, after which it again increases. At higher temperatures the minimum is displaced toward lower concentrations and finally disappears. The negative viscosity effect decreases rapidly with increasing temperature and in most cases disappears in the neighborhood of 30°. At still higher temperatures the viscosity effect becomes positive. In general, the positive viscosity effect increases markedly with the temperature.

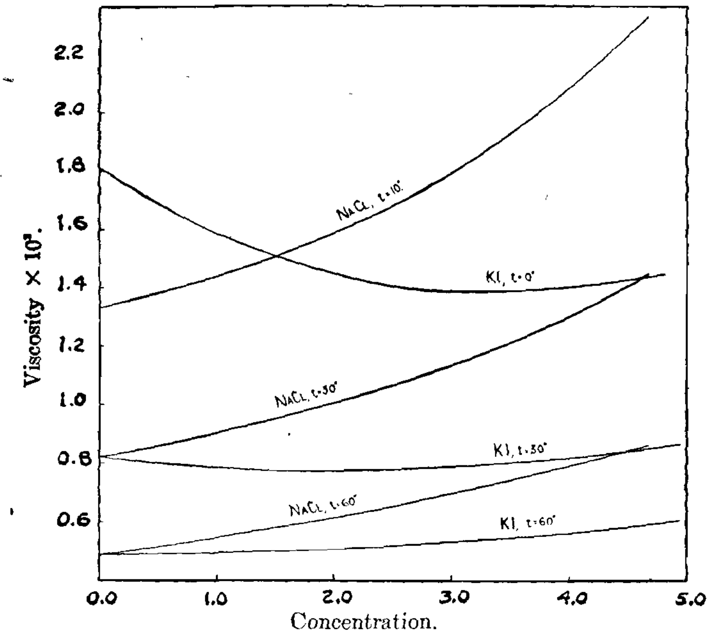

FIG. 16. Viscosity of Aqueous Solutions at Different Concentrations.

In glycerine solutions,[7] ammonium iodide, potassium iodide, and rubidium iodide exhibit negative viscosity effects. Lithium chloride, on the other hand, as in water, exhibits a viscosity increase with increasing concentration. In glycerine solutions, the negative viscosity effect disappears in the neighborhood of 75°.

It is obvious that, if the viscosity of a solution changes with concentration, the speed of the carriers, to which the conductance of the solutions is due, will likewise change with the concentration. If this is the case, then the conductance ratio, $\gamma = \frac{\Lambda}{\Lambda_o}$, no longer measures correctly

[7] Davis and Jones, *Ztschr. f. phys. Chem. 81*, 68 (1913).

the degree of ionization. It has been proposed to take account of the change of conductance due to the viscosity effect in direct proportion to the fluidity change of the solution.[8] In that case the degree of ionization of the electrolyte is given by the expression:

$$\gamma = \frac{\Lambda}{\Lambda_0}\frac{F_0}{F}, \tag{40}$$

where F_0 is the fluidity of the pure solvent and F that of the solution. Other writers [9] have proposed an equation of the form:

$$\gamma = \frac{\Lambda}{\Lambda_0}\left(\frac{F_0}{F}\right)^p, \tag{41}$$

where p is a constant, and Λ and Λ_0 are ionic conductances. If p were equal to unity, the conductance of the solution would be corrected in direct proportion to the fluidity change. Difficulty arises in determining the value of p. It has been suggested that the value of this constant may be derived from the manner in which the speed of an ion in dilute solution changes as a function of the temperature. As we shall see presently, the change in the Λ_0 values of the ions is not in general directly proportional to the fluidity change of the solvent, but is in most cases smaller. It has been shown that a relation of the type

$$\Lambda = KF^p \tag{42}$$

holds very nearly.[10] The values of the constant p for different salts are given in Table XLII.

TABLE XLII.

VALUE OF THE VISCOSITY-TEMPERATURE EXPONENT p FOR DIFFERENT IONS.

Univalent Ions.

Ion	Cl^-	K^+	NH_4^+	NO_3^-	Ag^+	Na^+	CH_3COO^-
p	.88	.887	.891	.807	.949	.97	1.008
Λ	65.4	64.7	64.4	61.8	54.	43.5	34.6

Divalent Ions.

Ion	$1/2\,SO_4^{--}$	$1/2\,C_2O_4^{--}$	$1/2\,Ba^{++}$	$1/2\,Ca^{++}$
p	0.944	.931	.986	1.008
Λ	68.7	63.8	55.9	52.1

[8] Bousfield and Lowry, *Phil. Trans.* [A] *204*, 289 (1903); Noyes and Falk, *J. Am. Chem. Soc. 34*, 454 (1912).
[9] Washburn, *J. Am. Chem. Soc. 33*, 1463 (1911).
[10] Johnston, *J. Am. Chem. Soc. 31*, 1010 (1909).

Since p is in general less than unity, it follows that the conductance of the ions changes less rapidly than does the viscosity of the solvent for a given increase in temperature. As a rule, the lower the conductance of the ion, the greater the value of the exponent p. For most slowly moving ions the exponent appears to approach the value unity as a limit. This is exemplified in the case of the acetate and the calcium ions. The lower the conductance of an ion, therefore, the more nearly does the conductance change in direct proportion to the fluidity change of the solvent. But while the value of p in Equation 42 has thus been evaluated, there is no good reason for believing that the exponent p in Equation 41 will have the same value. It obviously is not possible to determine the manner in which correction should be applied for the change in the conductance of solutions due to concentration change, unless we know the manner in which the ionization at these concentrations varies as a function of concentration. In other words, the nature of the correction as found will depend upon the assumed nature of the conductance function.

We have the equation:

$$\frac{C\gamma^2}{1-\gamma} = K' = f(C),$$

where $f(C)$ is some function of the concentration of the solution. As we have seen, in solutions at higher concentrations, the function K' follows approximately the relation:

$$\frac{(C\gamma)^n}{C(1-\gamma)} = D, \tag{9a}$$

where n has a value in the neighborhood of 1.5 for aqueous solutions. Assuming this equation to hold at higher concentrations, we may determine the nature of the viscosity correction on the basis of this assumption. In order to determine the nature of the correction, therefore, we may determine the value of the constants n and D at lower concentrations, where the viscosity change is negligible, and thereafter extrapolate this function to higher concentrations. In other words, by means of Equation 9a we may calculate the value of γ at higher concentrations and compare it with the directly measured value and with the fluidity of the solution at that concentration. Or, conversely, the experimentally determined conductance values at higher concentrations may be multiplied by an assumed correction factor and the corrected values compared with the values calculated by means of the above equation. If the assumptions made are applicable, then the two values should correspond.

The simplest correction would be that in which the conductances were assumed to change in direct proportion to the fluidity change of the solution.

This method of correction has been applied to solutions of potassium iodide dissolved in water at 0°.[11] In Figure 17, lower curve, are plotted values of log $(C\Lambda)$ and of $\log[C(\Lambda_0 - \Lambda)]$, both for the measured (rep-

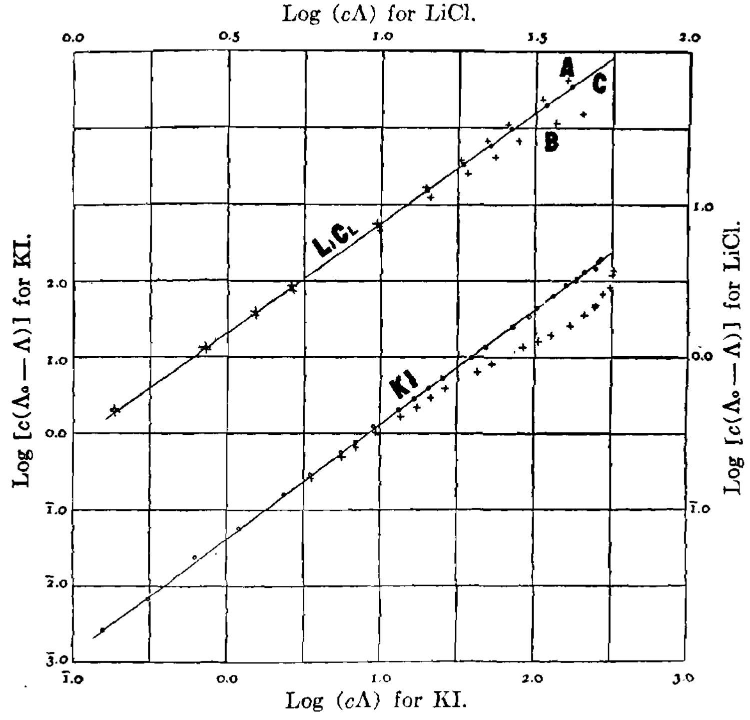

FIG. 17. Showing Influence of Viscosity Correction on the Conductance Curves of KI and LiCl in Water at 0°.

resented by crosses) and the corrected (represented by circles) conductance values of potassium iodide dissolved in water at 0°. If Equation 9a holds and if the assumed viscosity correction is applicable, then the corrected points should lie upon a straight line.[12] This, apparently, is the case.

The conductance curve of potassium iodide in water at 0° is a very exceptional one in that at higher concentrations it passes through a slight minimum and maximum, after which the conductance decreases very rapidly with increasing concentration. This form of the curve is due

[11] Kraus, *J. Am. Chem. Soc.* *36*, 35 (1914).
[12] Equation 9a may be written: $n \log (C\Lambda) = \log [C(\Lambda_0 - \Lambda)] + \log D\Lambda_0^{m}$.

to the viscosity change of the solution at higher concentrations. As we have seen, the fluidity passes through a maximum, after which it decreases sharply. If the values of the conductance as calculated from Equation 9a are multiplied by the fluidity ratio $\frac{F}{F_0}$, then these calculated values fall upon a curve (B) exhibiting a slight maximum and minimum,

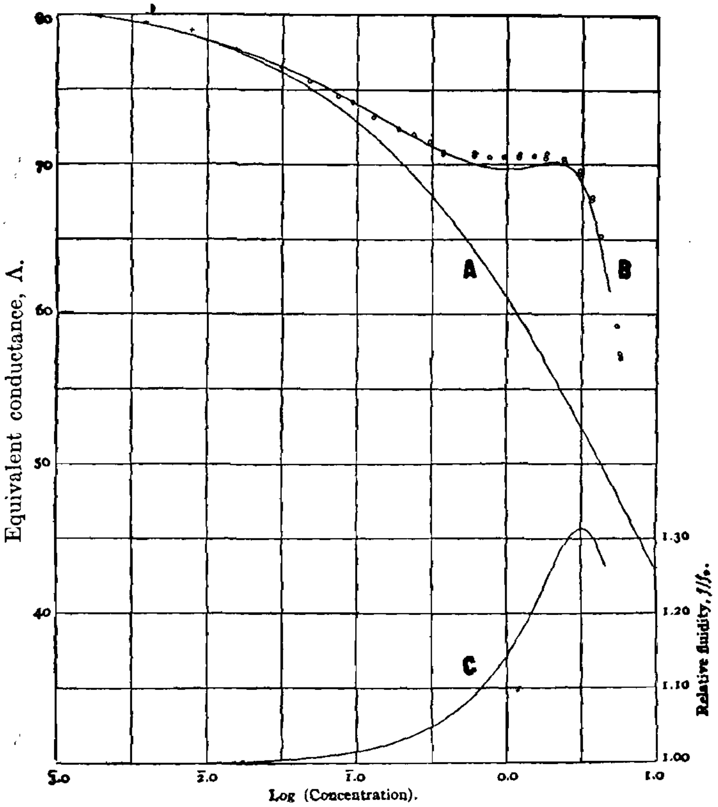

FIG. 18. Showing the Influence of Fluidity Change on the Conductance Curve of KI in Water at 0°.

which practically coincides with the curve of measured conductances, as may be seen from Figure 18. It is apparent that in the case of solutions of potassium iodide in water—and, in fact, this has been shown to be true for aqueous solutions of all electrolytes exhibiting a negative viscosity effect—the speed of the ions changes in direct proportion to the fluidity change of the solution. The peculiar form of the conductance curve, as we have it in solutions of the potassium iodide, is due to the variation of the viscosity effect.

In solutions of electrolytes in water which exhibit a positive viscosity effect, the conductance appears to change less than the viscosity of the solution. If we treat the conductance curve of lithium chloride in a manner similar to that employed in the case of potassium iodide, we obtain as plot not a straight line, but a curve lying below the straight line resulting from Equation 9a. In other words, the conductance values appear to be overcorrected. This result is illustrated in Figure 17, upper curve, in which A is the uncorrected curve, B is the curve in which the conductance is corrected in direct proportion to the fluidity change, while C is a curve in which correction has been applied to the lithium ion only. We may conclude, therefore, that, in aqueous solutions, the conductance may be corrected for the viscosity change in direct proportion to the fluidity change in the case of salts which exhibit a negative viscosity effect, but that, in solutions of salts which exhibit a positive viscosity effect, the correction made should be smaller. Just what corrections should be applied is difficult to determine at the present time.

We have seen that in non-aqueous solutions the viscosity effect is much larger than it is in aqueous solutions. We should therefore expect that the conductance of non-aqueous solutions would be affected to a much greater extent than that of aqueous solutions. It appears, however, that in solutions of electrolytes in non-aqueous solvents the conductance changes much less than the fluidity of the solvent.

The relation between the conductance and the viscosity is illustrated in Figure 19, in which are plotted the conductance and fluidity values of solutions of potassium iodide in liquid ammonia at different concentrations. Branch B is extrapolated on the assumption that Equation 9a holds. There is also indicated on this figure the calculated conductance of these solutions, Branch D, on the assumption that the conductance changes in direct proportion to the fluidity of the solvent. It will be observed that the conductance, as corrected in this way, is much too low to correspond with the experimental conductance curve represented by circles. It is evident, therefore, that in non-aqueous solutions the conductance change is smaller than corresponds to the viscosity change. This is further borne out by the fact that Equation 11 appears to hold for solutions of many electrolytes up to concentrations at times as high as 2 normal. It is obvious that the viscosity of the solutions at these concentrations must be much greater than that of the pure solvent, and consequently it follows that the correction to be applied for the viscosity change is probably the smaller the greater the viscosity change; that is, the lower the dielectric constant of the solvent. On the other hand, it has been found, in the case of all solutions in non-aqueous solvents, that,

at sufficiently high concentrations, the conductance curve ultimately falls, and falls the more rapidly the higher the concentration. There appears to be no exception to this behavior. There can be little question but that the final decrease in the conductance is due to a large increase in the viscosity of the medium. This is illustrated in Figure 20, where the conductance of solutions of silver nitrate in methylamine[13] is represented as a function of the concentration. The maximum lies a little

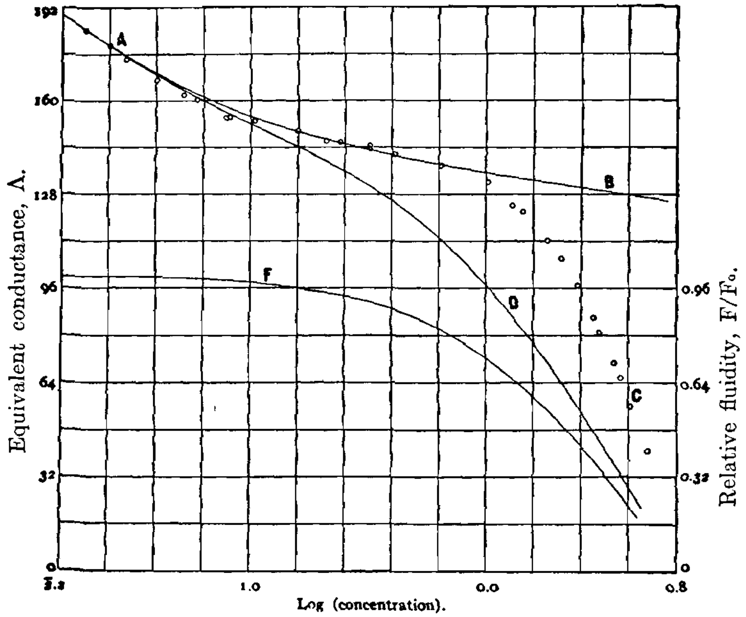

FIG. 19. Showing the Influence of Fluidity Change on the Conductance of Solutions of KI in NH_3 at $-33.5°$.

above normal concentration at $-33°$ and is displaced toward higher concentrations at higher temperatures.

3. *Relation between Viscosity and Conductance on the Addition of Non-Electrolytes.* The addition of a non-electrolyte to a solution of an electrolyte in most cases increases the viscosity of the solution.[14] The conductance change on the addition of a non-electrolyte is in the same direction as that of the viscosity change, but in most cases the conductance change is smaller than the corresponding viscosity change.

[13] Fitzgerald, *loc. cit.*, p. 640.

[14] In a few instances, however, where *the added non-electrolyte forms a stable complex* with one of the ions in solution, the addition of a non-electrolyte results in a viscosity decrease. An example of this effect is found in solutions of certain of the heavy metals in water whose viscosity is reduced on the addition of ammonia. [Blanchard, *J. Am. Chem. Soc. 26*, 1315 (1904).] In these cases the addition of a non-electrolyte causes a decrease in the viscosity only so long as it combines with the electrolyte to form the complex. Beyond this point the viscosity in general increases with further addition of non-electrolyte.

The experimental material available is very incomplete. So far as any conclusion may be drawn, however, the conductance change is the more nearly proportional to the fluidity change, the smaller the molecules of

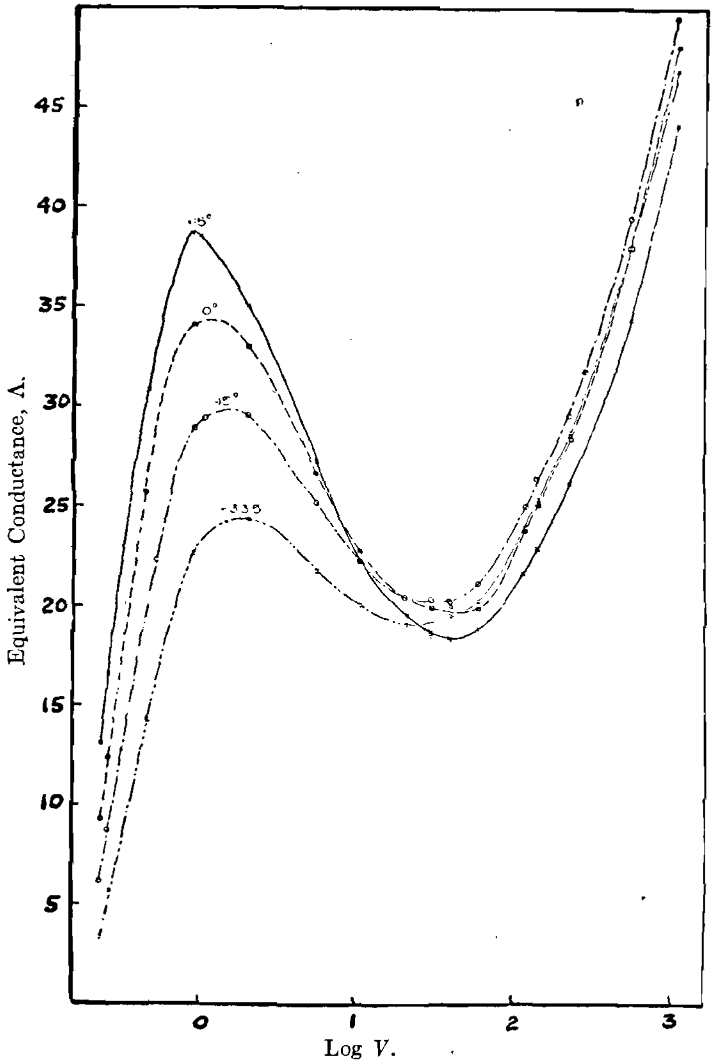

Fig. 20. Conductance of Silver Nitrate in Methylamine at Different Temperatures.

the added non-electrolyte. It has been found that the relation between the conductance and the viscosity on the addition of a non-electrolyte may be expressed by an exponential equation of the form $\Lambda_0 = KF^p$, where Λ_0 is the limiting conductance of the electrolyte in solutions con-

taining the non-electrolyte and F is the fluidity of the solution. The smaller the conductance change of the electrolyte for a given fluidity change, the smaller is the value of the exponent p.

In Table XLIII are given values of the exponent p for aqueous solutions of a number of electrolytes in the presence of non-electrolytes.

TABLE XLIII.

CHANGE OF CONDUCTANCE OF ELECTROLYTES DUE TO ADDED NON-ELECTROLYTES.

Non-Electrolyte	Sucrose†	Raffinose*	Glycerol†	Acetone ‡	Urea†	Methyl Alcohol*
Mol. Wt.	342.1	594.4	92	58	60	32
p for KCl	0.66	0.675	0.83	0.93	0.95	1.2
t	20°	25°	20°	25°	25°	25°

Non-Electrolyte	Sucrose†	Raffinose*	Raffinose*	Methyl Alcohol*	Methyl Alcohol*
Electrolyte	HCl	CsCl	LiCl	CsCl	LiCl
p	0.55	0.676	0.669	0.8	1.1
t	25°	25°	25°	25°	25°

Non-Electrolyte	Acetone‡	Glycerol§	Urea§	Pyridine§
Electrolyte	HCl	$CuSO_4$	NaOH	$LiNO_3$
p	1.0	1.0	1.0	1.0–1.3
t	25°	15°	—	25°

* Clark, Thesis, Univ. of Ill. (1915). See also, Washburn, "Principles of Physical Chemistry," 2 Ed., p. 260.
† Öholm, *Finska Vetenskap. Soc. Förhandl.* 55, A No. 5, p. 75 (1913); Washburn, *loc. cit.*
‡ Ryerson, Thesis, Univ. of Ill. (1915).
§ Green, *J. Chem. Soc.* 93, 2049 (1908).

It will be seen from the table that, in general, the higher the molecular weight of the added non-electrolyte, the smaller is the value of the exponent p. This is most clearly shown in the case of potassium chloride, for which electrolyte the data are more extensive than for others. The exponent in the presence of sucrose and raffinose is in the neighborhood of 0.67, while in the presence of urea it is 0.95 and in the presence of methyl alcohol 1.2. The molecular weight of the added electrolyte is thus a governing factor in determining the manner in which the conductance of an ion varies due to viscosity change. That some transpositions in the order of the exponent and in that of the molecular weight of the added non-electrolyte will occur is to be expected, since specific influences may make themselves felt. It is noticeable that in the case of methyl alcohol the exponent has a value greater than unity.

The significance of this result remains uncertain. It is to be expected, however, that, on the addition of an electrolyte whose molecular weight is lower than the mean of that of the solvent molecules, effects may occur which cannot well be predicted on the basis of our present knowledge of the viscosity relations in such mixtures. It is interesting to note that, in the presence of non-electrolytes of high molecular weight, the coefficient for different electrolytes has very nearly the same value. Thus, in the presence of raffinose the values of the exponent for lithium, potassium and caesium chlorides are very nearly identical. Since these salts have a common anion, it may be inferred that the influence of the viscosity effect due to non-electrolytes of high molecular weight is the same for the lithium, potassium and caesium ions. This is apparently not so nearly true in the presence of non-electrolytes of low molecular weight, but even here, in some instances at any rate, the exponent does not differ greatly for different salts. It would seem that the influence of the viscosity change on the conductance of an ion, due to the electrolyte itself, differs markedly from that due to the addition of a non-electrolyte. At the present time, sufficient data are not available to enable us to draw conclusions with any considerable degree of certainty.

4. *The Influence of Temperature on the Conductance of the Ions.* As is shown in Table XLII, with increasing temperature the conductance of the ions increases, and this increase is the more nearly proportional to the increase in the fluidity of the solvent, the lower the conducting power of the ion. In the case of the acetate ion, the conductance is everywhere proportional to the fluidity of water from 0° to 156°, which is the entire interval over which the viscosity of the solvent has been measured. In the following table are given the ratios of the fluidity of water to the conductance of the acetate ion from 0° to 156°.[15]

TABLE XLIV.

RATIO OF THE FLUIDITY OF WATER TO THE CONDUCTANCE OF THE ACETATE ION AT DIFFERENT TEMPERATURES.

Temp.	0°	18°	25°	50°	75°	100°	128°	156°
$\frac{F}{\Lambda_{CH_3COO^-}}$	2.73	2.72	2.73	2.72	2.71	2.72	2.71	2.71

It is evident that, in dilute solutions, the conductance of the acetate ion, and presumably therefore its speed, is directly proportional to the fluidity of the solvent.

Since the conductance of the acetate ion is proportional to the fluidity

[15] Johnston, *loc. cit.*

of water up to 156°, we may assume, in the absence of experimental data, that it remains proportional at higher temperatures. In order, therefore, to compare the conductance of the different ions with the fluidity of water, we may compare the conductance of these ions with that of the acetate ion whose values are known up to 306°. The ratio of the conductances of the various ions to that of the acetate ion is given in Table XLV.[16]

TABLE XLV.

INFLUENCE OF TEMPERATURE ON THE CONDUCTANCE OF VARIOUS IONS RELATIVE TO THAT OF THE ACETATE ION.

Ion	Conductance at temperatures:—									
	0.0°	18°	25°	50°	75°	100°	128°	156°	218°	306°
K^+	1.99	1.87	1.83	1.72	1.66	1.58	1.54	1.50	1.32	1.18
Na^+	1.28	1.26	1.25	1.22	1.20	1.19	1.19	1.18	1.15	1.11
NH_4^+	1.98	1.86	1.83	1.72	1.66	1.59	1.55	1.52	1.37	1.30
Ag^+	1.62	1.57	1.54	1.51	1.49	1.45	1.43	1.42	1.29	..
Cl^-	2.02	1.89	1.85	1.73	1.67	1.59	1.54	1.51	1.32	1.18
NO_3^-	1.99	1.78	1.73	1.55	1.46	1.37	1.30	1.25	1.21	..
H^+	11.82	9.08	8.58	6.95	5.88	4.95	4.23	3.68	2.79	1.82
OH^-	5.17	4.95	4.71	4.24	3.75	3.38	3.07	2.81	2.08	1.62

In determining the conductance of the various ions, it is of course necessary to assume values for the transference numbers of one pair of ions. In the case of potassium chloride, the transference number is very nearly 0.5 and at higher temperatures it appears to approach this value as a limit. It has been assumed, therefore, that at temperatures above 100° the transference number of the potassium and chloride ions is 0.5. This assumption, moreover, is justified by the fact that, as the temperature increases, the transference numbers of all ions appear to approach one another. In the above table the ionic conductances at the higher temperatures are based upon this assumption.

The relation between the ionic conductances and the temperature is shown in Figure 21, where the conductances relative to the acetate ion are plotted as ordinates and the temperatures as abscissas. Since the conductance of the acetate ion is proportional to the fluidity of the solvent, it follows that the ordinates will be proportional to the ratio of the ionic conductances to the fluidity of the solvent. On examining the figure, it will be seen that the greater the value of the conductance of an ion, the less does the conductance increase as the temperature increases. That is, the ratio $\frac{\Lambda_i}{\Lambda_{ac}}$ decreases with increasing temperature and de-

[16] Kraus, *loc. cit.*

creases the more, the greater the value of the ratio. In other words, these ratios appear to approach unity, as a limit at high temperatures. The conductances of all ions, therefore, appear to approach that of very slowly moving ions. For example, at 0° the conductance of the hydrogen ion is 11.82 times that of the acetate ion, while at 306° it is only 1.82 times that of this ion. At 0° the conductance of the potassium ion is 1.99 times that of the acetate ion, while at 306° it is only 1.18 times that of this ion. At 0° the conductance of the sodium ion is 1.28 times that of the acetate ion, whereas at 306° it is only 1.11 times that of the same

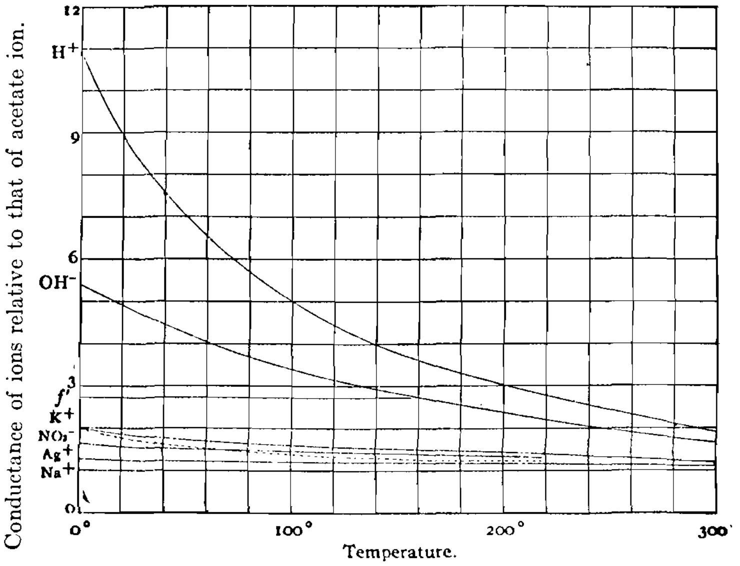

Fig. 21. Showing the Relative Change of Ionic Conductances with Temperature.

ion. It is evident, therefore, that as the temperature increases the speeds of the different ions approach a common value. With the exception of the nitrate ion, the curves for the ionic conductances do not intersect. At low temperatures, however, the relative conductance of the nitrate ion, with respect to that of the acetate ion, decreases much more rapidly than it does for other ions having the same conducting power. At 0° the ratio of the conductance of the nitrate ion to that of the acetate ion is 1.99, whereas at 25° it is only 1.73. In the case of the potassium ion at the lower temperature, the ratio is also 1.99, but at 25° it is 1.83.

These results have an important bearing on our conceptions as to the nature of the conducting particles, particularly as regards the effect of temperature on the speed of these particles. As has been shown by

means of transference experiments, the ions are hydrated in water. In order to account for the fact that the speeds of the different ions at higher temperatures approach one another, it might be assumed that the hydrates break down at higher temperatures, but this assumption would not be in harmony with certain facts. Since the conductance of the slowly moving ions changes in direct proportion to the fluidity of the solvent as the temperature increases, it is reasonable to assume that the relative dimensions of the ion complex remain practically constant. If, therefore, the speed of the more rapidly moving ions approaches that of the more slowly moving ions at higher temperatures, it points to a slowing up of the more rapidly moving ions as the temperature increases. This corresponds to a greater relative resistance to their motion, which can only be interpreted as due to an increase in the dimensions of the ion-complex. In other words, as the temperature increases, the hydration of the more rapidly moving ions increases, which tends to reduce their speed relative to that of more slowly moving ions.

If the hydration of the ions is due primarily to electrical forces acting between the ions, which are charged, and the surrounding solvent molecules, which have an electrical moment, then we should expect that, as the dielectric constant of the medium decreases, the size of the complex will increase, since in a dielectric medium the force is inversely proportional to the dielectric constant. For this reason we should expect the relative speeds of ions in non-aqueous solvents of low dielectric constant to approach one another much more nearly than they do in water. This appears to be the case. Moreover, this is also in harmony with the fact that in the case of very large ions, in other words, in the case of ions which have a low conducting power, the conductance in different solvents, as well as at different temperatures, is very nearly proportional to the fluidity of the solvent. We may conclude, therefore, that the hydration of the ions increases, or, including non-aqueous solvents, that the solvation of the ions increases with the temperature because of a decrease in the dielectric constant of the medium. It is not to be assumed, however, that the dimensions of the ions in different solvents are controlled entirely by the dielectric constant. The solvent may combine chemically with a given ion to form a complex, which ion in turn may have associated with it additional solvent molecules, due to electrical interaction between this ion and the solvent. We should expect this to be the case with silver ions which form an extremely stable complex with ammonia. Even in aqueous solutions, the silver ion forms a complex $Ag(NH_3)_2^+$ with ammonia. This may account for the relatively low conducting power of the silver ion in liquid ammonia solution. Whereas,

for example, the conductance of the lithium ion in ammonia is 3.36 times that of the lithium ion in water, that of the silver ion in ammonia is only 2.15 times that in water. So, also, we find that the ammonium ion in ammonia has a conductance of only 2.03 times that of the ammonium ion in water, indicating the formation of relatively large complexes. In this connection it may be pointed out that the ammonium salts form with ammonia saturated solutions whose vapor pressures are extremely low. For example, the vapor pressure of a saturated solution of ammonium nitrate in ammonia is one atmosphere at 26°.

If the complexity of the ions increases with the temperature, we should expect that at higher temperatures the viscosity would be increased more largely for a given addition of salt than at lower temperatures. This, again, corresponds with observations on the viscosity of solutions. The change of viscosity due to a given addition of salt increases as the temperature rises, and this increase appears to be the greater the higher the temperature. It is to be noted, also, that the increase in viscosity due to the addition of electrolytes is much greater than that due to the addition of non-electrolytes, except in the case of non-electrolytes which have very large molecules. In general, as has already been pointed out, the viscosity effect is the greater the lower the dielectric constant of the solvent. In solvents of very low dielectric constant, the viscosity of some solutions becomes so great, at high concentrations, that they often become practically solid.

5. *The Influence of Pressure on the Conductance of Electrolytic Solutions.* As we have seen, the conductance of the ions is a function of the viscosity of the solution. As the hydrostatic pressure on a solution is increased, its viscosity changes, the sign and magnitude of this change being dependent upon the nature of the solvent medium and upon the concentration of the solution in question. The effect of pressure on the viscosity of solutions in water, as well as the effect upon water itself, has been measured by Cohen.[17] In Figure 22 are shown the percentage changes of viscosity for pure water at different pressures and temperatures. From an inspection of the figure it will be seen that with increasing pressure the viscosity of water decreases markedly. As the temperature rises, however, the viscosity effect diminishes and it is evident that at higher temperatures the effect changes sign. From the form of the curves at 15° and 23° it is evident that at higher pressures the curves for the viscosity effect will pass through a minimum and that ultimately, therefore, the viscosity change will change sign, the viscosity increasing with increasing pressure. In non-aqueous solvents

[17] Cohen, *Wied. Ann.* *45*, 666 (1892).

the viscosity increases with increasing pressure, as was found by Röntgen [18] and Warburg and Sachs [19] for ether and benzene, and by Cohen for turpentine. In general, the viscosity effect in non-aqueous solvents is greater than that in water, and, as we shall see below, the effect is the greater the greater the viscosity of the medium.

The pressure-viscosity effect in solutions is a function of the con-

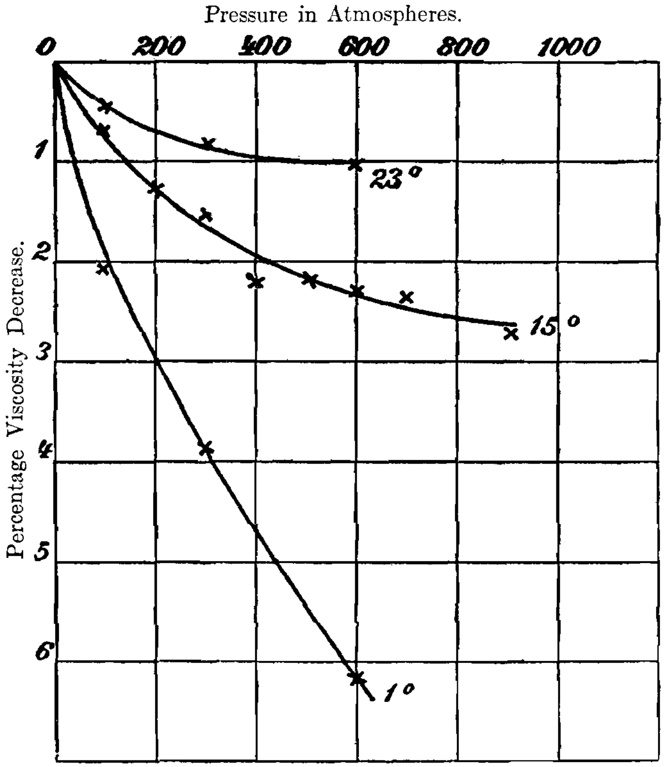

FIG. 22. Showing the Influence of Pressure on the Viscosity of Water at Different Temperatures.

centration, as was shown by Cohen. In Figure 23 are shown curves for the viscosity change of solutions of sodium chloride in water at 2° and 14.5°. The broken line curves relate to the lower temperature. The concentrations of the various solutions are indicated on the figure. With increasing concentration of the solution, the viscosity decrease, due to a given increase in pressure, diminishes and ultimately changes sign; that is, with increasing pressure, the viscosity of the solution increases. The lower the temperature, the greater the influence of a given pressure

[18] Röntgen, *Wied. Ann.* 22, 510 (1884).
[19] Warburg and Sachs, *Wied. Ann.* 22, 518 (1884).

change upon the viscosity, but at higher concentrations the effect of temperature diminishes greatly.

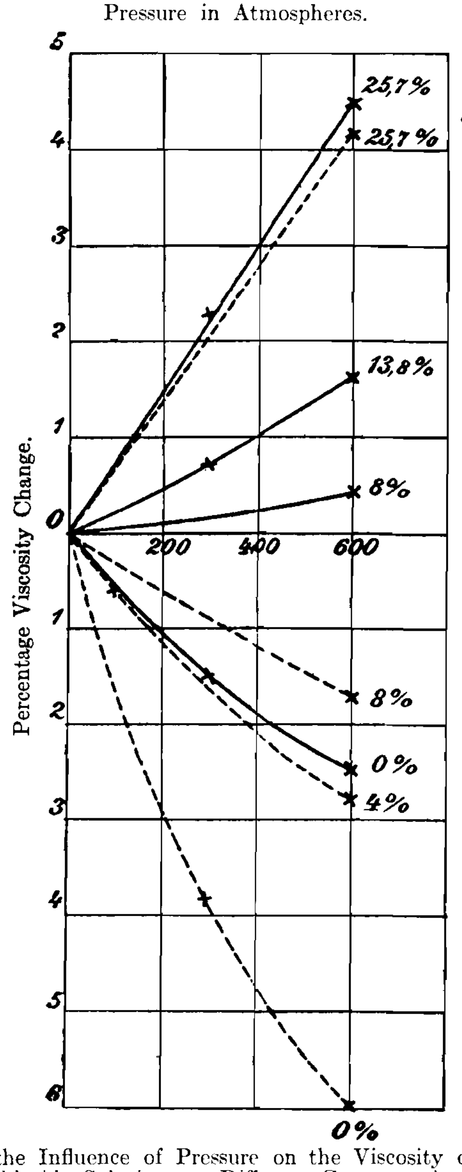

FIG. 23. Showing the Influence of Pressure on the Viscosity of Aqueous Sodium Chloride Solutions at Different Concentrations.

The change in the viscosity of a solution with pressure will obviously have an influence upon the conductance of the solution. The viscosity

effect, however, is not the only one involved. As Tammann has shown,[20] the conductance-pressure coefficient is the resultant sum of four effects; namely, the volume change of the solution due to pressure change, the change in the mobility of the ions due to the viscosity change of the solution, the change in the ionization of the electrolyte, and finally the change in the conductance of the solvent medium, which, as a rule, is due to a small quantity of electrolyte present as impurity. The conductance-pressure coefficient, therefore, is given by the equation:

$$\frac{1}{\lambda}\frac{\Delta\lambda}{\Delta p}=\frac{1}{v}\frac{\Delta v}{\Delta p}+\frac{1}{\varphi}\frac{\Delta\varphi}{\Delta p}+\frac{1}{\gamma}\frac{\Delta\gamma}{\Delta p}+\frac{\lambda'}{\lambda}\frac{1}{\gamma'}\frac{\Delta\gamma'}{\Delta p} \tag{43}$$

where λ is the conductance of the solution due to the electrolyte, λ' that due to the solvent medium, γ is the ionization of the electrolyte and γ' that of the solvent medium, and φ is the ionic resistance; that is to say, the reciprocal of the ionic mobility. In the equation, therefore, the first term of the right-hand member measures the conductance change due to the volume decrease of the solution; the second term measures the conductance change due to the viscosity change of the solution; the third, the conductance change due to the ionization change of the electrolyte; and the last term, the conductance change due to the ionization change of the solvent medium. By suitably choosing the condition of the solution, it is possible to minimize the value of various of the terms entering into this equation, and thus make apparent the effect of the various factors on the conductance of the solution due to pressure change.

Let us examine first the typical form of the conductance-pressure curves in the case of aqueous solutions of 0.01 N KCl. In Figure 24 [21] are represented values of the ratio of the resistance of the solution, R_p, under a pressure of p kilograms per square centimeter to the resistance $R_{p=1}$ under a pressure of one atmosphere at a series of temperatures. It will be observed that as the pressure increases the resistance of the solution decreases initially. As the temperature rises, the value of the decrease due to a given pressure change diminishes. At high pressures the isotherms exhibit a minimum. The higher the temperature, the lower the pressure at which the minimum occurs. It is evident that at sufficiently high temperatures the minimum will disappear and the resistance of the solution will increase throughout with increasing pressure. This has been found to be the case with strong electrolytes, such as sodium chloride in aqueous solution.

In solutions of strong binary electrolytes, the ionization at a concentration of 0.01 N is so high that but little change is to be expected in

[20] Tammann, *Ztschr. f. phys. Chem.* 27, 458 (1898).
[21] Körber, *Ztschr. f. phys. Chem.* 67, 222 (1909).

its value as a result of pressure change. The third term of the right-hand member of Equation 43 may therefore be neglected. The fourth term, likewise, may be neglected at this concentration, since the conductance of the pure solvent is negligible in comparison with that of the solution. The observed conductance change of solutions, under these conditions, therefore, is due to the first two terms. The value of the first

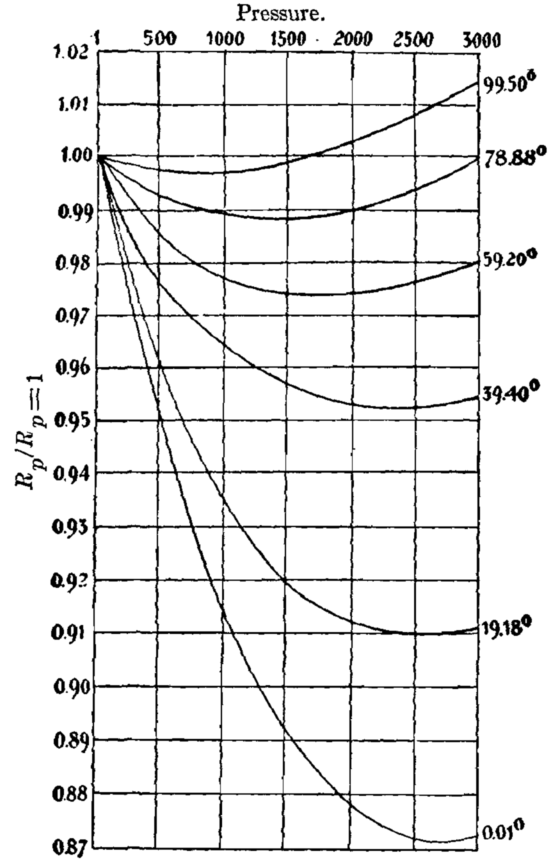

FIG. 24. Showing the Influence of Pressure on the Resistance of 0.01 N Aqueous KCl Solutions at Different Temperatures.

term of the right-hand member may be calculated from the data of Amagat on the compressibility of pure water, since the compressibility of an 0.01 N solution will not differ appreciably from that of pure water. If the first term of the right-hand member is transposed, we have the equation:

$$\frac{1}{\varphi}\frac{\Delta\varphi}{\Delta p} = \frac{1}{\lambda}\frac{\Delta\lambda}{\Delta p} - \frac{1}{v}\frac{\Delta v}{\Delta p}, \tag{44}$$

from which equation the effect of pressure upon the conducting power of the ions may be determined. In a solution at a concentration of 0.01 N the effect of pressure on the viscosity will not differ materially from that on the pure solvent. It might be expected that the effect of pressure on the conductance of the ions would vary inversely as the viscosity change of the solution. Indeed, Tammann, on comparing the conductance-pres-

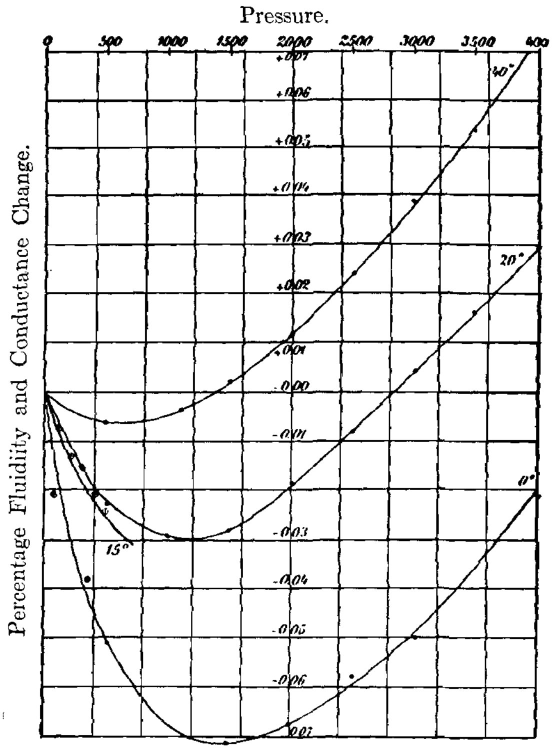

FIG. 25. Comparison of the Influence of Pressure on the Conductance and the Fluidity of Dilute Aqueous NaCl Solutions at Different Temperatures.

sure effects as calculated according to Equation 44 for 0.1 N sodium chloride with the measured viscosity effects of Cohen, found almost an exact correspondence as may be seen from Figure 25.[22] The points on this figure represented by combined cross and circle are measured viscosity values of Cohen, while the curves represent the values of the viscosity effect as determined from conductance measurements according to Equation 44. Measurements by Körber,[23] while confirming the results of Tammann for sodium chloride, show that the viscosity-conductance effect due to pressure in the case of different electrolytes is a function

[22] Tammann, *Wied. Ann.* 69, 773 (1899).
[23] Körber, *Ztschr. f. phys. Chem.* 67, 212 (1909).

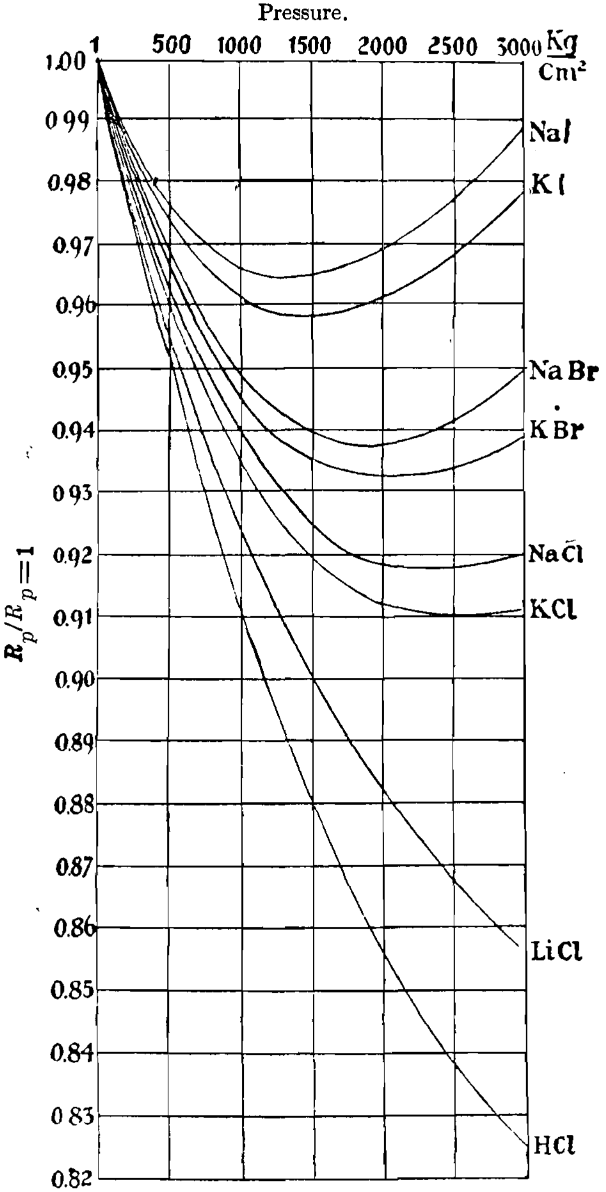

FIG. 26. Influence of Pressure on the Resistance of 0.01 N Solutions of Different Salts in Water at 19.18°.

of the nature of the ions and that the correspondence found for sodium chloride is purely accidental.

In Figure 26 are represented values of the ratio $\frac{R_p}{R_{p=1}}$ for aqueous

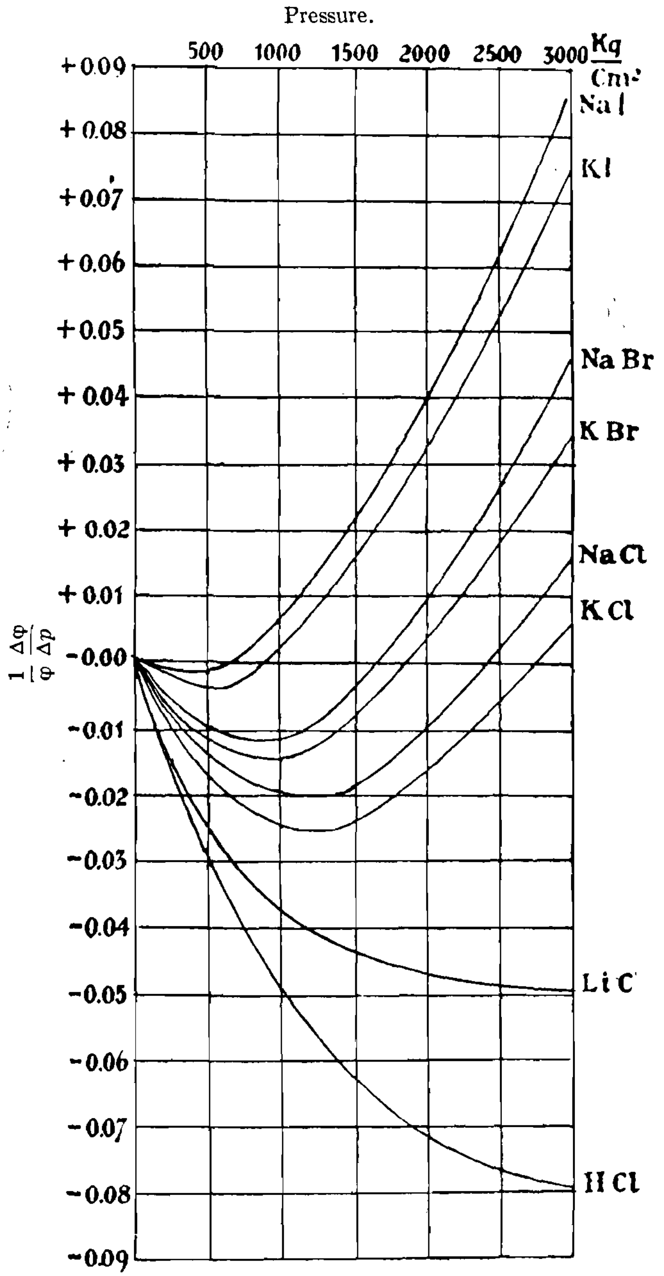

FIG. 27. Showing the Influence of Pressure on the Resistance Coefficients for Aqueous Solutions of Various Electrolytes.

solutions of various electrolytes at a concentration of 0.01 N at a temperature of 19.18°, while in Figure 27 [24] are shown values of $\frac{1}{\varphi}\frac{\Delta\varphi}{\Delta p}$ as calculated from the measured values of $\frac{R_p}{R_{p=1}}$, according to Equation 44. As stated above, the curve for sodium chloride corresponds with the viscosity curve of pure water as determined by Cohen. It will be seen, however, that the curves for other electrolytes differ from that of sodium chloride and that, therefore, in these cases the pressure effect upon the ions is not directly proportional to the viscosity change of the solution. In the case of potassium chloride the conductance evidently increases slightly more than corresponds to the viscosity change of the solution, while for lithium chloride and hydrochloric acid the conductance increase due to increasing pressure is enormously greater than the viscosity change of the solution. On the other hand, in the case of potassium bromide, sodium bromide, potassium iodide, and sodium iodide the conductance change of the electrolytes is much smaller than the corresponding viscosity change of the solution. Manifestly, the change in the speed of the ions with pressure change is dependent not only on the viscosity of the solvent medium, but also on other factors. What these factors are, we do not know with certainty, but it appears probable that the speed of the ions is affected by a change in their effective size. Such an effect will obviously be a property of the ions themselves, which is in accordance with Körber's observations. However we may interpret these results, it is obvious that the speed of the ions in a dilute aqueous solution is not determined primarily by the viscosity of the solution, although the viscosity is an important factor.

According to Equation 43, the value of the ratio $\frac{R_p}{R_{p=1}}$ varies as a function of concentration. In Figure 28 [25] are shown values of the ratio $\frac{R_p}{R_{p=1}}$ for sodium chloride in water at 19.18° at a series of concentrations. At the highest concentrations the resistance of the solution increases throughout with increasing pressure. This is in accord with Cohen's observations on the viscosity of sodium chloride solutions, which, at higher concentrations, exhibit a marked viscosity increase. As the concentration of the solution decreases, the curves exhibit a minimum. Initially, with increase in pressure, the resistance of the solution decreases,

[24] Körber, *loc. cit.*, p. 227.
[25] *Ibid.*, *loc. cit.*, p. 234.

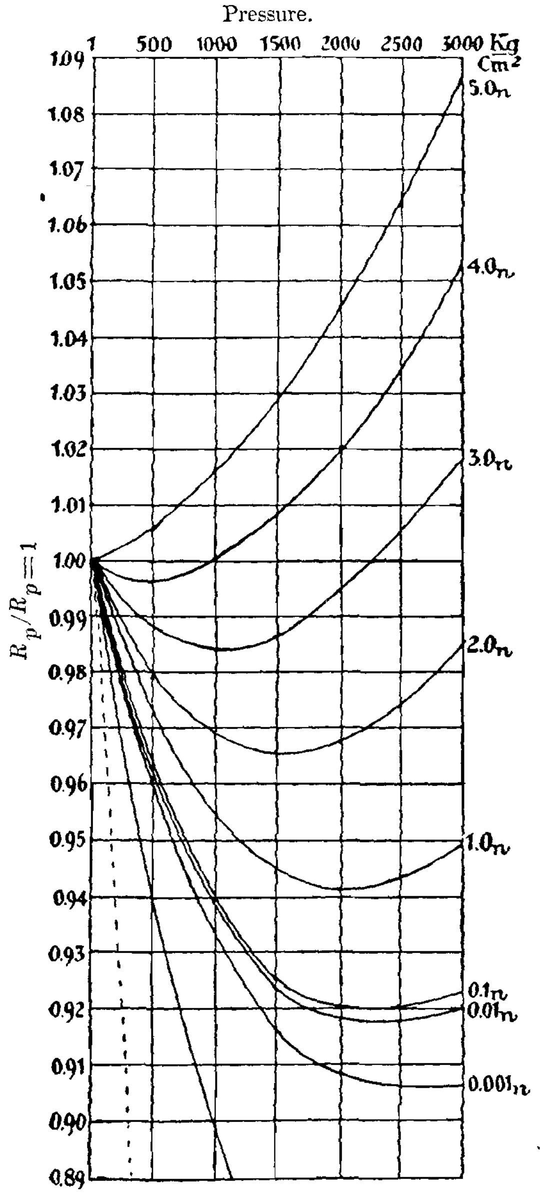

FIG. 28. Showing the Influence of Pressure on the Resistance of Sodium Chloride Solutions at Different Concentrations at 19.18°.

while at higher pressures the resistance of the solution increases. In this case, again, the general form of the curve corresponds to the viscosity

effects of the solution. As the concentration decreases, the minimum point is displaced toward higher pressures, and the curves approach one another. Thus the curves at 0.1 N and 0.01 N differ but little. This is due to the fact that below a concentration of 0.1 N the ionization of the electrolyte is so great and the concentration so low that the viscosity effects could not differ materially from those in pure water. At lower concentrations, namely at 10^{-3} N and 10^{-4} N, the minimum disappears and the pressure effect becomes very large, the curves becoming the steeper, the lower the concentration of the solution. This divergence of the curves at very low concentrations is due to the effect of pressure on the conductance of the solvent medium; namely, to the fourth term in Equation 43. In the limit, these curves approach the dotted curve shown in the figure, which is that of the solvent medium.

We have still to consider the case in which the third term of Equation 43 becomes an effective factor. This will obviously be the case with solutions of weak electrolytes. The ionization of an electrolyte, if the mass-action law holds—and this is in general the case with weak electrolytes in aqueous solutions—is determined by the value of its ionization constant K. According to the Planck equation, we have:

$$\frac{d \log K}{dp} = - \frac{\Delta v}{RT}. \tag{44a}$$

According to Tammann, the value of Δv is negative, so that as the result of pressure increase the value of the ionization constant K increases and with it the value of the ionization γ. In the case of weak electrolytes, at intermediate concentrations and lower temperatures, the first three terms of Equation 43 have the same sign, and consequently the resistance of solutions of weak electrolytes should decrease with increasing pressure much more largely than that of solutions of strong electrolytes under otherwise the same conditions, and the decrease should be the greater the weaker the electrolyte and the greater the value of Δv. The first investigations in this direction were carried out by Fanjung.[26] Measurements on 0.1 N acetic acid were carried out by Tammann up to pressures of approximately 4000 kilograms per square centimeter. In the following table are given values of the ratio $\frac{R_p}{R_{p=1}}$ for acetic acid at 20.14°.[27]

In the case of ammonia, which has approximately the same ionization constant as acetic acid, the pressure effect is even greater than in that of

[26] Fanjung, *Ztschr. f. phys. Chem.* *14*, 673 (1894).
[27] Tammann, *Wied. Ann.* *69*, 770 (1899).

acetic acid, since the value of Δv for ammonia is more than twice that of acetic acid.

TABLE XLVI.

RELATIVE RESISTANCE OF 0.01 N SOLUTIONS OF ACETIC ACID IN WATER AT 20.14° AT DIFFERENT PRESSURES.

$\frac{p \text{ kg.}}{\text{cm.}^2}$	$\frac{R_p}{R_{p=1}}$
1	1.000
500	0.855
1000	0.738
1500	0.650
2000	0.582
2500	0.526
3000	0.487
3500	0.447
4000	0.410

The influence of pressure upon the conductance of electrolytes is brought out more clearly by representing the conductance-pressure coeffi-

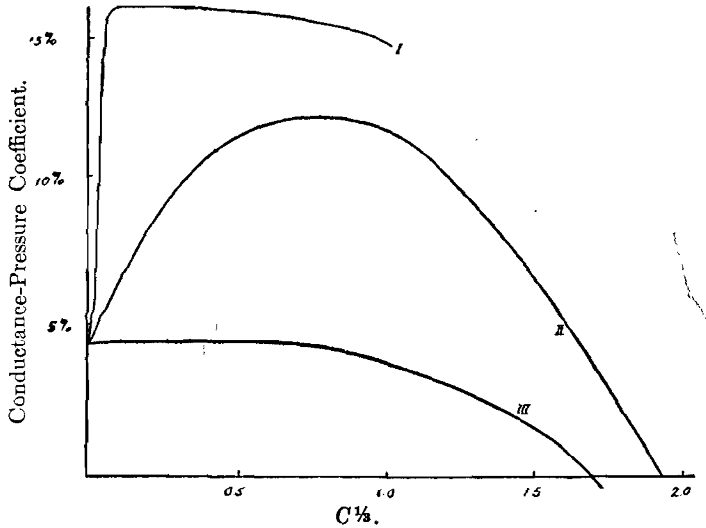

FIG. 29. Conductance-Pressure Coefficients for Electrolytes of Different Types as a Function of Concentration at a Pressure of 500 kg./cm.^{2}.
Curve 1, Weak Electrolytes.
Curve 2, Moderately Strong Electrolytes.
Curve 3, Strong Electrolytes.

cient as a function of the concentration of the solution, the pressure remaining constant. In Figure 29 [28] Curve 1 represents the pressure

[28] Tammann, *Ztschr. f. phys. Chem.* 17, 729 (1895).

coefficient of weak electrolytes as a function of their concentration at a pressure of 500 kg./cm.[2] The curve actually corresponds very closely with that of acetic acid in water at this pressure. As Tammann has shown, it follows from the Planck equation that at low concentrations and for relatively small values of the constant K the ionization change, due to increasing pressure, increases with increasing concentration, until a practically constant value is reached. The conductance-pressure coefficient increases with increasing concentration of the weak electrolyte up to a concentration of about 10^{-3} normal for electrolytes whose constant is below 10^{-4}. At higher concentrations the ionization change due to pressure change remains practically constant. However, at higher concentrations the value of $\frac{1}{v}\frac{\Delta v}{\Delta p}$ decreases, while the value of $\frac{1}{\varphi}\frac{\Delta \varphi}{\Delta p}$ decreases and ultimately changes sign, as follows from Cohen's observations on the viscosity of aqueous salt solutions. Therefore, the conductance-concentration curves, and consequently the curves for the coefficient, exhibit a very flat maximum. In the case of solutions of strong electrolytes, the term $\frac{1}{\gamma}\frac{\Delta \gamma}{\Delta p}$ has inappreciable values at concentrations below 10^{-2} normal, and has only very small values at much higher concentrations. In dilute solutions, therefore, the pressure coefficient has very nearly a constant value, independent of concentration. At higher concentrations, however, the value of the coefficient decreases, owing to the diminution in the value of $\frac{1}{v}\frac{\Delta v}{\Delta p}$ and owing to an ultimate change in the sign of the viscosity effect at higher concentrations of the electrolyte, as was found by Cohen. Electrolytes of intermediate strength exhibit a type of curve intermediate between these two extreme types, as represented by Curve 2. In this case the value of the coefficient increases with increasing concentration of the solution at lower concentrations owing to the increasing ionization of the electrolyte. Ultimately, however, the effect of the viscosity change makes itself felt, the curve passes through a maximum, and thereafter falls with increasing concentration. At very low concentrations the viscosity-pressure coefficient has actually been found to increase and approach large values due to the effect of the fourth term in the right-hand member of Equation 43. This increase in the coefficient, as was shown by Tammann,[29] is due to the increased ionization of the solvent medium.

The limiting value which the coefficient $\frac{1}{\lambda}\frac{\Delta \lambda}{\Delta p}$ approaches at low con-

[29] Tammann, *Ztschr. f. phys. Chem.* 27, 464 (1898).

centrations, assuming that the conductance of the solvent is zero, or has been otherwise corrected for, differs for different electrolytes, and is, in general, the greater, the greater the value of $\frac{R_p}{R_{p=1}}$. Thus the limit approached for hydrochloric acid at a pressure of 3000 kilograms per square centimeter is approximately 17 per cent, while that of sodium chloride is approximately 8 per cent and that of potassium chloride 9 per cent. Since in dilute solution the effect due to $\frac{1}{v}\frac{\Delta v}{\Delta p}$ is the same as that in pure water, it follows that these differences are due to differences in the viscosity effect as illustrated in Figure 28. In the case of hydrochloric acid, the value of $\frac{1}{\lambda}\frac{\Delta\lambda}{\Delta p}$ passes through a flat maximum at a concentration in the neighborhood of 0.5 normal.

In non-aqueous solutions the order of the viscosity effects differs from that in aqueous solutions, chiefly owing to the fact that with increasing pressure the viscosity of the solvent medium increases and consequently the speed of the ions is reduced with increasing pressure. In Figure 30 [30] are shown values of the ratio $\frac{R_p}{R_{p=1}}$ for solutions of 0.002 N tetramethylammonium iodide and 0.1 N malonic acid in ethyl alcohol. As was the case with water, the curve for weak electrolytes lies below that for strong electrolytes. With increasing temperature, however, the order of the curves is reversed with respect to their order in water; that is, the ratio $\frac{R_p}{R_{p=1}}$ decreases both in the case of strong and weak electrolytes. The curves are very nearly linear for solutions of strong electrolytes but are convex toward the axis of pressures for solutions of weak electrolytes. This form of the curve is accentuated in solutions in solvents of high viscosity; as, for example, amyl alcohol, for which values of $\frac{R_p}{R_{p=1}}$ are represented in Figure 31.[31] In this case, the curves for malonic acid at higher temperatures exhibit a minimum, while the curves for tetramethylammonium iodide are distinctly convex toward the axis of pressures. It is evident that at pressures beyond 3000 kilograms per square centimeter the curve for malonic acid in ethyl alcohol would likewise pass through a minimum. The observed phenomena in non-

[30] Schmidt, *Ztschr. f. phys. Chem.* 75, 319 (1910).
[31] *Ibid., loc. cit.*, p. 320.

aqueous solutions may be accounted for in the same manner as those for aqueous solutions. The difference in the form of the curves for various electrolytes in the two cases arises chiefly as a result of the difference

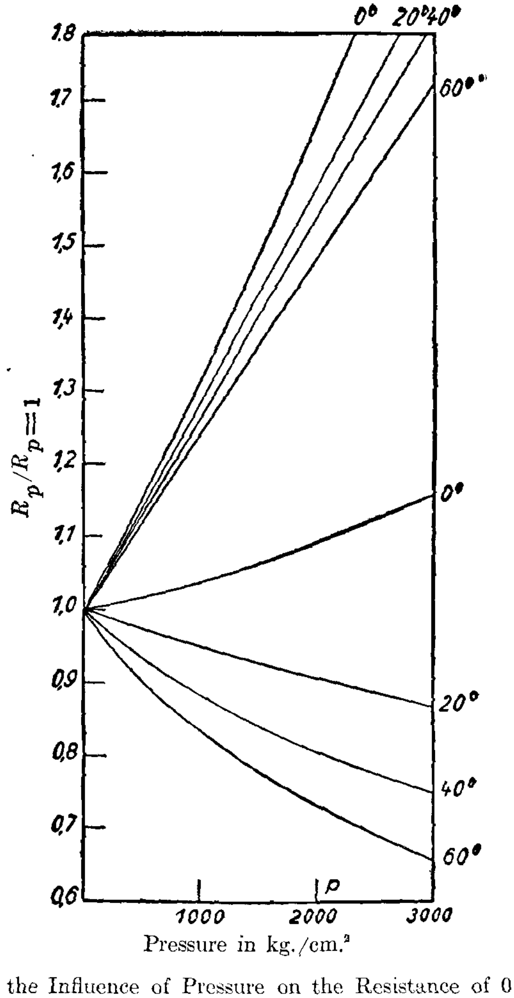

FIG. 30. Showing the Influence of Pressure on the Resistance of 0.002 N Solutions of Tetramethylammonium Iodide (above) and 0.1 Malonic Acid (below) in Ethyl Alcohol at Different Temperatures.

in the sign and magnitude of the viscosity pressure effect and in the value of the ionization of the dissolved electrolytes. In solvents of lower dielectric constant, the typical salts behave like electrolytes of intermediate strength. At a given pressure, with increasing concentration of

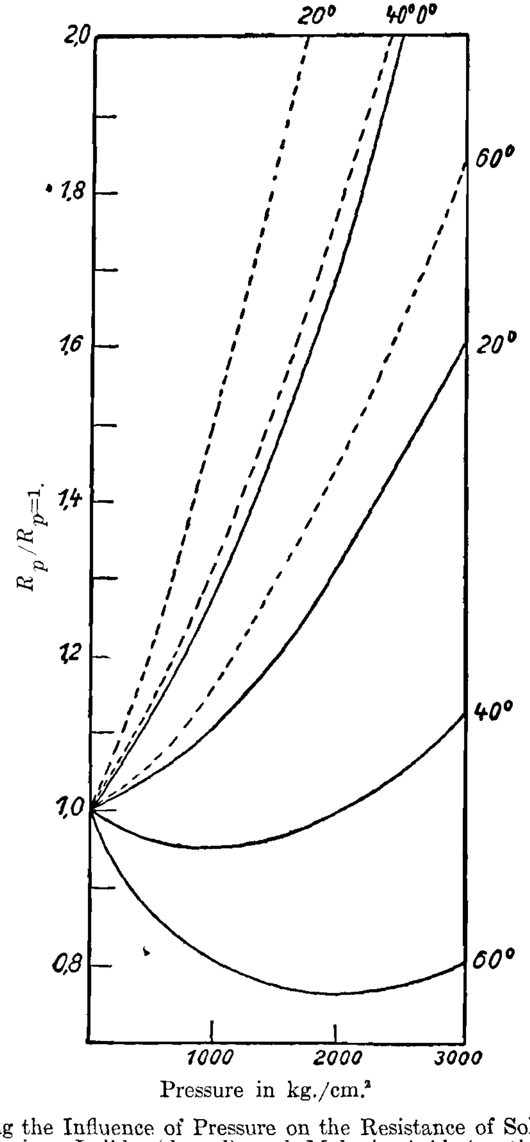

FIG. 31. Showing the Influence of Pressure on the Resistance of Solutions of Tetramethylammonium Iodide (dotted) and Malonic Acid (continuous) in Amyl Alcohol at Different Temperatures.

the electrolyte, the ratio $\frac{\lambda p}{\lambda_{p=1}}$, due to the increased ionization of the electrolyte, increases from values less than unity to greater values which are in general less than unity. At still higher concentrations, however,

the increasing viscosity effect overbalances the effect of increased ionization and the curve passes through a maximum. In solutions of weak electrolytes the ratio $\frac{R_p}{R_{p=1}}$ increases rapidly with increasing concentration of the electrolyte, due to increased ionization, and, for very weak electrolytes, particularly at low temperatures, passes through unity to greater values. Here, again, at sufficiently high concentrations, the curve may pass through a maximum, owing to the ultimate predominance of the viscosity effect. From his measurements, making the assumption that the Planck equation holds as well as certain other assumptions, Schmidt has calculated the value of $\frac{\varphi_p}{\varphi_{p=1}}$, the viscosity ratio, due to pressure, for potassium iodide, sodium iodide and tetramethylammonium iodide in alcohol. He found that this ratio increases markedly with the pressure. In the case of potassium iodide and sodium iodide the increase is very nearly the same, being from 1.0 to 2.34 for 0.02 N solutions and a pressure change from 1 to 3000 atmospheres. In the case of tetramethylammonium iodide the ratio $\frac{\varphi_p}{\varphi_{p=1}}$ increases somewhat more than for the other two electrolytes measured. This indicates that the viscosity effect in alcohol, similar to that in water, is a property of the ions. It appears, however, that the effects in the case of different ions are much more nearly the same in non-aqueous solutions than in water. This is as might be expected, since in solvents of low dielectric constant the ionic conductances themselves differ much less than in water. Schmidt has also calculated the value of the ionization γ at different pressures and has found that the ionization increases with increasing pressure.

That the pressure effect is intimately related to the viscosity of the solution is clearly indicated by the fact that the order of the effects in different solvents corresponds to the order of the viscosities of these solvents. The higher the viscosity of the solvent, the greater is the ratio $\frac{R_p}{R_{p=1}}$ for a given pressure change. In the majority of solvents Schmidt found that this ratio might be expressed as a function of the pressure by the equation:

$$\log \frac{R_p}{R_{p=1}} = \beta p, \tag{45}$$

where β is a constant. This equation was found to be particularly applicable at higher temperatures. In other cases it was necessary to add

a quadratic term to the right-hand member of the equation. In the case of non-associated liquids the value of β may be expressed in terms of the viscosity of the solvent by means of the equation:

$$\beta = 0.000106 + 0.00561\,\varphi, \tag{46}$$

where φ is the viscosity of the solvent. In the following table are given values of the viscosity φ, together with the measured values of β and those calculated according to Equation 46.[32]

TABLE XLVII.

RELATION BETWEEN THE VISCOSITIES OF DIFFERENT SOLVENTS AND THE PRESSURE EFFECTS.

Solvent	φ	β	β calc.
Normal solvents.			
Anisaldehyde	0.056	0.0_3420	0.0_3420
Benzylcyanide	0.022	0.0_3234	0.0_3229
Nitrobenzene	0.020	0.0_3217	0.0_3218
Furfurol	0.017	0.0_3204	0.0_3201
Benzaldehyde	0.016	0.0_3194	0.0_3196
Acetic anhydride	0.010	0.0_3178	0.0_3162
Acetone	0.003	0.0_3106	0.0_3123
Associated solvents.			
Glycerine	7.0	0.0_3300	0.0_393
Isoamyl alcohol	0.042	0.0_3178	0.0_3342
Ethyl alcohol	0.012	0.0_3095	0.0_3173
Methyl alcohol	0.006	0.0_3078	0.0_3140

The calculated and observed values of β agree very well for the non-associated solvents, but in the case of the associated solvents there is a wide discrepancy between the two. A very simple relation thus exists between the viscosity and the pressure effect in the case of normal solvents, while in the case of associated solvents the relation is much more complex. This is as might be expected, for in associated solvents a change in the complexity of the solvent molecules doubtless accompanies any pressure change. It is clear that the difference in the nature of the pressure effects in water and in non-aqueous solvents is chiefly due to the difference in the viscosity effects in these cases.

[32] Schmidt, *loc. cit.*, p. 334.

Chapter VI.

The Conductance of Electrolytic Solutions as a Function of Temperature.

1. *Form of the Conductance-Temperature Curve.* The limiting value of the conductance is a function of the viscosity of the solvent, and consequently of the temperature also. The conductance of the more slowly moving ions is very nearly proportional to the fluidity of the solvent over such ranges of temperature for which viscosity data are available. The conductance of the more rapidly moving ions increases relatively less with the temperature than does that of the more slowly moving ions, and this effect is the more marked the greater the conductance of the ions.

In considering the conductance of solutions at higher concentrations, it is necessary to take into account another factor, namely the change in the ionization of the electrolyte. The observed conductance change is therefore the resultant effect due to the change in the viscosity of the solution and to the change in the ionization of the electrolyte. While, with increasing temperature, the viscosity decreases and the conductance consequently increases, the ionization in general decreases and the conductance of the electrolyte decreases in consequence. Since these two factors affect the conductance in opposite directions, it follows that the resultant effect of temperature on the conductance will depend on the relative magnitude of the ionization and the viscosity effects; and, in general, with increase in temperature the conductance of a solution may either increase or decrease. At ordinary temperatures, the conductance of many solutions increases with the temperature, and it was formerly assumed that a positive temperature coefficient was a characteristic property of electrolytic solutions. We now know, however, that this is not the case and that the temperature coefficient of solutions may be either positive or negative and that, in a given solvent, the temperature coefficient is a function of the temperature as well as of concentration, and that the sign of the temperature coefficient may change with temperature as well as with concentration.

Considering, first, the conductance as a function of temperature, the concentration remaining fixed, it is found that, in general, the conductance increases with the temperature at low temperatures; but as the

temperature rises, the temperature coefficient decreases. The conductance curve is therefore concave toward the axis of temperatures. If the temperature is carried sufficiently high, the conductance passes through a maximum after which it decreases, the negative temperature coefficient increasing as the temperature rises. Experiments of this kind were first carried out by Sack,[1] who found that, in solutions of copper sulphate,

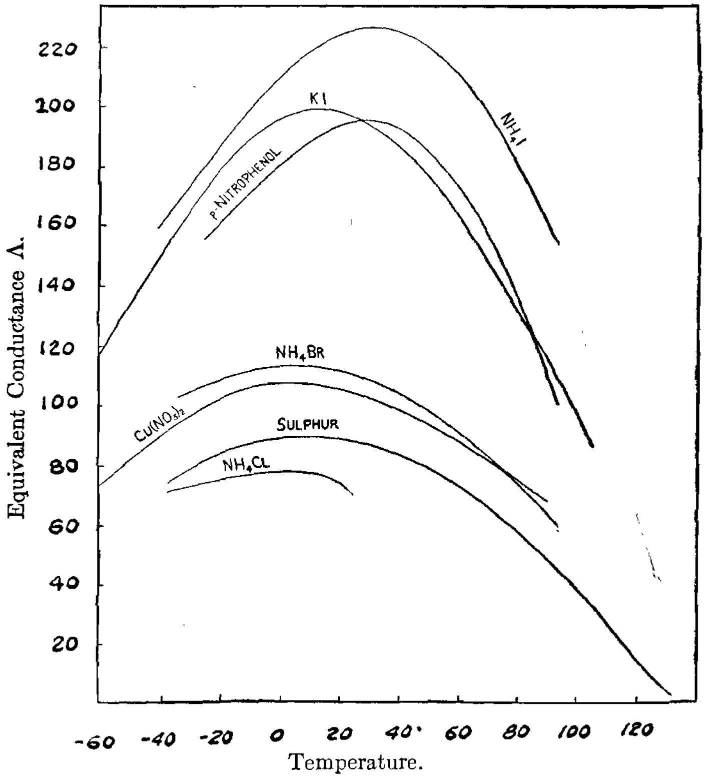

FIG. 32. Conductance-Temperature Curves for Various Electrolytes in Liquid Ammonia.

the conductance passes through a maximum in the neighborhood of 128°. For solutions of strong binary electrolytes in water, however, the maximum lies at much higher temperatures.

Before proceeding to a detailed discussion of aqueous solutions, we may consider solutions in other solvents. The conductances of a considerable number of solutions in ammonia have been measured and a maximum has been found in all cases.[2] The form of the curves will be

[1] Sack, *Wied. Ann. d. Phys.* *43*, 212 (1891).
[2] Franklin and Kraus, *Am. Chem. J.* *24*, 83 (1900).

evident from Figure 32. As a rule the maximum lies in the neighborhood of 25° C but the temperature of the maximum is a function of concentration and with increasing concentration the maximum is displaced toward lower temperatures. The curves for different electrolytes are similar, indicating that the underlying phenomenon is the same in all cases. As the critical temperature is approached, the conductance approaches a very low value, and it appears as though the curve would cut the axis of temperatures at a point near the critical temperature. The conductance, however, does not, in fact, fall to zero at the critical point, but has appreciable values at temperatures much above that point. The phenomenon in the neighborhood of the critical point will be discussed in detail in another section and need not be further considered here. It may be stated, however, that the property of forming conducting solutions with electrolytes is not peculiar to the liquid state but is one common to fluid systems.

The form of the conductance-temperature curve is the same in all solvents. The conductance of a considerable number of solutions in sulphur dioxide has been measured[3] at higher temperatures and the curves obtained have a form which corresponds with those of ammonia solutions. In solutions of KI in methylamine the form of the curve differs slightly in that, at very high temperatures, the conductance appears to approach the axis of temperatures asymptotically. In the alcohols,[4] as well as in water,[5] the conductance-temperature curves are of the same general type.

2. *Conductance of Aqueous Solutions at Higher Temperatures.* In order to proceed with the discussion of this subject, it is necessary to have some notion as to the degree of ionization of the electrolyte in solution. The degree of ionization of non-aqueous solutions at higher temperatures is unknown. In other words, we do not have a sufficient number of measurements at a series of temperatures and concentrations to enable us to determine the value of Λ_0 at these temperatures. For aqueous solutions, however, a large amount of material is available, having been obtained by A. A. Noyes and his associates,[6] and from these data the effect of temperature on the ionization of salts becomes apparent.

In the following table are given values of the equivalent conductance for potassium chloride at a series of temperatures and at the concentrations 0.08 and 0.002 normal.

[3] Walden and Centnerszwer, *Ztschr. f. phys. Chem.* *39*, 542 (1902).
[4] Kraus, *Phys. Rev.* *18*, 40 and 89 (1904).
[5] Noyes, Carnegie Publication, No. 63, pp. 47, 103, and 266.
[6] Noyes, *loc. cit.*

TABLE XLVIII.

CONDUCTANCE OF KCl IN H_2O AT HIGHER TEMPERATURES.

Concentration	t	0°	18°	25°	100°	140°	156°	218°	281°	306°
0.08 N.	Λ	72.3	113.5	—	341.5	455	498	638	723	720
0.002 N.	Λ	79.6	126.3	146.4	393	534	588	779	930	1008

It will be noted that at the higher concentration the conductance passes through a maximum somewhere between 281° and 306°. In the more dilute solution, a maximum has not been reached below 306°. This behavior is quite general in aqueous solutions and is found also in non-aqueous solutions. The lower the concentration, the higher the temperature of the maximum.

For solutions of sodium chloride, the conductance-temperature curve is similar to that of potassium chloride, although for this salt the maximum has not been reached at 306°, even at a concentration of 0.08 normal. We have seen that, with increasing temperature, the conductance of the sodium ion increases relatively more than that of the potassium ion. As a consequence, the maximum in the conductance curve is shifted to higher temperatures. In general, the higher the conductance of the electrolyte, the lower the temperature of the maximum and the lower the concentration at which the maximum will appear at a given temperature.

For silver nitrate, the maximum lies somewhat lower than it does for potassium chloride, as may be seen from the following table:

TABLE XLIX.

CONDUCTANCE OF $AgNO_3$ IN H_2O AT HIGH TEMPERATURES.

Concentration	t	18°	100°	156°	218°	281°	306°
0.08 N	Λ	96.5	294	432	552	614	604

The lower temperature of the maximum for silver nitrate is due, partly, to the abnormal manner in which the conductance of the nitrate ion changes as a function of the temperature and, partly, to the more rapid decrease in the ionization of silver nitrate with increasing temperature.

The higher types of salts exhibit maxima which are more pronounced and which occur at lower concentrations and lower temperatures. In Table L are given values for barium nitrate and magnesium sulphate at 0.08 normal.

TABLE L.

CONDUCTANCE OF $Ba(NO_3)_2$ AND $MgSO_4$ IN H_2O AT HIGH TEMPERATURES.

Barium Nitrate.

Concentration	Temp.	18°	100°	156°	218°	281°
0.08 N	Λ	81.6	257.5	372	449	430

Magnesium Sulphate.

	Temp.	18°	100°	156°	218°
0.08 N	Λ	52	136	133	75.2

It will be observed that the maximum lies below 281° for barium nitrate, while for magnesium sulphate the maximum lies between 100° and 156°. The more complex the salt the lower the temperature and the lower the concentration at which the maximum appears. As we shall see presently, this is due chiefly to the fact that the ionization of salts of higher type falls off more rapidly with the temperature than does that of the binary salts. For strong acids, the maxima lie at temperatures considerably below those of the binary salts. For hydrochloric acid the maximum lies in the neighborhood of 240° and for nitric acid in the neighborhood of 200° at a concentration of 0.08 N.

The conductance-temperature curve of sulphuric acid, which is a dibasic acid, has a peculiar form, which has an important significance. Below are given values of the equivalent conductance for sulphuric acid at a series of temperatures at concentrations 0.002 and 0.08 normal.

TABLE LI.

CONDUCTANCE OF H_2SO_4 AT HIGH TEMPERATURES.

Concentration	18°	25°	50°	75°	100°	128°	156°	218°	306°
0.002 N	353.9	390.8	501.3	560.8	571.0	551	536	563	637
0.08 N	240	258	306	342	373	408	440	488	474

It will be observed that, at the higher concentration, sulphuric acid exhibits a relatively flat maximum at a temperature of about 250°, while at the lower concentration it exhibits a maximum at about 100° and a minimum at about 160°, after which the conductance again increases and presumably passes through a maximum at a temperature above 306°. At still lower concentration the maxima and minima become more pronounced. As Noyes and Eastman[7] pointed out, this behavior of sulphuric acid appears to be due to the fact that ionization takes place in two stages according to the equations:

[7] Noyes, *loc. cit.*, p. 270.

$$H_2SO_4 = H^+ + HSO_4^-$$
$$HSO_4^- = H^+ + SO_4^{--}$$

At the higher concentrations, the second ionization process has taken place to only a small extent and the form of the curve is largely due to the change in the ionization according to the first process, the maximum point occurring when the increased conductance of the ions due to temperature is just counterbalanced by the decreased conductance due to decrease in ionization. At the lower concentration the second ionization process is likewise involved. The second ionization corresponds to that of the weaker acid and the ionization according to this process falls off more rapidly with rising temperature, thus giving rise to the initial maximum. When the ionization according to the second process has been largely depressed, the curve thereafter depends chiefly upon the ionization according to the first equation.

The ionization of strong electrolytes, apparently without exception, decreases with increasing temperatures; but at lower temperatures the rate of decrease is relatively small. In the case of the weak acids and bases the ionization increases between 0° and 40°, and thereafter decreases rapidly at higher temperatures. In the following table are given values for the ionization constants of ammonium hydroxide and acetic acid.[8] The values represent averages for a number of concentrations. In general, the ionization constant is independent of concentration up to 0.1 normal.

TABLE LII.

IONIZATION CONSTANT $\times 10^{-6}$ FOR AMMONIUM HYDROXIDE AND ACETIC ACID.

	18°	25°	218°	306°
NH_4OH	17.2	18.1	1.80	0.093
CH_3COOH........	18.3	—	1.72	0.139

Initially there is a slight increase in the ionization constant, after which there is a sharp decrease at higher temperatures. Between 218° and 306° the constant of ammonium hydroxide changes slightly more than that of acetic acid. Similar results have been obtained in the case of other weak acids. For example, the ionization constant of diketotetrahydrothiazole[9] at 0°, 18° and 25° is respectively 0.0711×10^{-6}, 0.146×10^{-6} and 0.181×10^{-6}. Between 0° and 25° the constant of ammonium hydroxide varies between 13.91 and 18.06×10^{-6}. It appears

[8] Noyes, *loc. cit.*, p. 234.
[9] *Ibid., loc. cit.*, p. 290.

that the change in the value of the constant is greater for the weaker electrolyte.

The ionization constant for water itself is a function of the temperature. At ordinary temperature the constant has been variously determined, the values at 18° lying between 0.68 and 0.80, the lower value being probably the more nearly correct.

In the following table are given values of the ionization constant of water at various temperatures up to 306°.[10]

TABLE LIII.

IONIZATION CONSTANT OF WATER AT DIFFERENT TEMPERATURES.

	0°	18°	25°	100°	156°	218°	306°
$K_W \times 10^{14}$ ...	0.089	0.46	0.82	48.	223.	461.	168.

The ionization constant of water thus increases very rapidly at lower temperatures and passes through a maximum not far from 218°. The large value of the ionization constant of water and the relatively low values of the ionization constants of the acids and bases at higher temperatures lead to a relatively large hydrolysis of the salts of anything but the strongest acids and bases, and it is not improbable that even salts of the strong acids and bases ultimately suffer hydrolysis at low concentrations at the highest temperatures.

The increase in the ionization constant of the weak acids between 0° and 40° may be related to the molecular changes which water undergoes within this temperature interval. Within this interval the density and specific heat of water are abnormal and within this temperature interval, also, the viscosity effects in solution, as well as the viscosity effects under pressure, exhibit abnormal relations, as has already been pointed out. An adequate explanation of these various phenomena, however, appears not to exist.

The ionization of different electrolytes in water at temperatures from 18° to 306° are given in Table LIV at concentrations of 0.01 and 0.08 normal. An examination of this table shows that the ionization of all electrolytes decreases markedly with the temperature, the decrease being the greater the higher the temperature and the higher the concentration. The ionization-temperature curves of different binary electrolytes correspond closely with one another, with the exception of the strong acids and silver nitrate. In the case of the last named salt, however, the ionization values at the highest temperatures are subject to large errors,

[10] Noyes, *loc. cit.*, p. 346.

TABLE LIV.—IONIZATION OF ELECTROLYTES IN WATER AT HIGH TEMPERATURES.

Substance	Concentration	18°		100°		156°		218°		281°		306°	
		0.01	0.08	0.01	0.08	0.01	0.08	0.01	0.08	0.01	0.08	0.01	0.08
HCl	0.01	97.1	..	95.0	..	93.6	..	92.2	..	..	..	82.	..
	0.08	..	93.2	..	89.7	..	87.2	..	82.5	..	..	..	60.
HNO_3	0.01	96.8	..	95.2	..	93.4	..	..	..	..	..	..	..
	0.08		92.6	..	89.0	..	85.3	..	75.	..	..	..	33.
$NaOH$	0.01	96.2	..	95.7	..	94.3	..	92.	..	..	..	..	..
KCl	0.01	94.2	..	91.1	..	89.7	..	89.8	..	87.	..	81.	..
	0.08	..	87.3	..	82.6	..	79.7	..	77.3	..	72.	..	64.
$NaCl$	0.01	93.6	..	92.7	..	92.1	..	90.2	..	84.	..	80.	..
	0.08	..	85.7	..	83.2	..	81.2	..	77.7	..	69.	..	63.
NH_4Cl	0.01	93.7	..	92.2	..	91.2	..	90.1	..	..	..	79.	..
$AgNO_3$	0.01	93.3	..	91.8	..	88.8	..	86.3	..	82.	..	77.	..
	0.08	..	83.3	..	80.2	..	75.8	..	70.8	..	64.	..	57.
$NH_4C_2H_3O_2$	0.01	91.9	..	88.7	..	87.1	..	..	..	..	..	..	..
$NaC_2H_3O_2$	0.01	91.2	..	88.8	..	88.0	..	82.2	..	..	..	76.	..
	0.08	..	81.1	..	77.6	..	75.6	..	68.5	..	..	..	..
$Ba(OH)_2$	0.01	93.	..	85.	..	85.	..	..	..	..	..	..	..
	0.08	..	83.	..	70.	..	65.	..	..	..	..	..	..
K_2SO_4	0.01	87.2	..	80.3	..	75.	..	63.	..	47.	..	37.	..
	0.08	..	73.2	..	64.8	..	58.	..	45.	..	31.	..	23.
$Ba(NO_3)_2$	0.01	86.7	..	83.6	..	80.	..	74.	..	59.	..	47.	..
	0.08	..	70.1	..	66.9	..	62.	..	53.	..	38.	..	..
H_2SO_4	0.01	83.	..	56.	..	49.	..	46.	..	..	..	..	..
	0.08	..	66.	..	48.	..	45.	..	42.	..	..	..	35.
$MgSO_4$	0.01	66.7	..	52.4	..	35.	..	13.	..	..	..	..	..
	0.08	..	45.5	..	31.9	..	19.	..	7.	..	..	..	..
H_3PO_4	0.01	60.	..	42.	..	29.4	..	..	..	..	..	..	..
	0.08	..	31.	..	19.5	..	12.5	..	..	..	..	..	..
$HC_2H_3O_2$	0.01	4.17	..	3.24	..	2.26	..	1.26	..	..	..	..	..
	0.08	..	1.50	..	1.17	..	0.82	..	0.46	..	..	..	0.14
NH_4OH	0.01	4.05		3.59	..	2.46	..	1.36	..	..	..	..	..
	0.08	..	1.45	..	..	..	..	..	0.47	..	..	..	0.11

owing to the possible hydrolysis of the salt, as well as to certain reactions which appear to take place in the solutions at the higher temperatures.[11] The ionization of hydrochloric and nitric acids falls off much more rapidly than does that of the salts and that of nitric acid falls off more rapidly than that of hydrochloric acid, as may be seen from Table LIV. At 0.08 normal and 306°, the ionization of nitric acid is only about one half that of hydrochloric acid. At that temperature the ionization of hydrochloric acid is approximately the same as that of the typical binary salts, such as potassium and sodium chlorides. The ionization of weak electrolytes, such as ammonium hydroxide and acetic acid, falls off much more rapidly than does that of the strong electrolytes. Correspondingly, at a given concentration, the maximum in the conductance-temperature curves occurs at lower temperatures in the case of weak acids and bases. For acetic acid this maximum lies in the neighborhood of 100°.

The ionization of salts of higher type, as well as that of the more complex acids and bases, such as sulphuric acid and barium hydroxide, falls off very markedly with the temperature, and the decrease is as a rule the greater the higher the type of the salt. This is well illustrated in the case of magnesium sulphate, whose ionization at 0.08 normal and 218° is only 7 per cent. Corresponding to this rapid decrease in the ionization of the more complex salts at the higher temperatures, the maximum in the conductance curves lies at relatively low temperatures.

As the temperature rises, the dielectric constant of water decreases and we should expect the properties of aqueous solutions to approach those of non-aqueous solutions. This is indeed the case. At higher temperatures, the ionization values for different electrolytes approach those of the same type of electrolytes in solvents of lower dielectric constants. The low ionization values of the salts of higher type correspond with the relatively low values of the ionization of the same type of salts in nearly all non-aqueous solvents. At 306°, many of the properties of electrolytic aqueous solutions, which differentiate these solutions from similar solutions in non-aqueous solvents, have in large measure disappeared. So, for example, the great difference in the conductance values of the different ions has almost completely disappeared at 306°. Similarly the abnormally high ionization values of hydrochloric and nitric acids, as well as of the strong bases, have disappeared at this temperature. And, finally, the ionization function, for the binary electrolytes at any rate, approaches values not very different from those of solutions in many non-aqueous solvents.

It is evident that, since the ionization decreases with the temperature,

[11] Noyes, *loc. cit.*, p. 94.

the value of the ionization function likewise decreases. It is interesting to examine the general course of the ionization function at different temperatures. In the following table are given values of the ionization function K' at a series of concentrations at 156° and 306°, for potassium chloride, and at 156°, 218° and 306° for nitric acid.

TABLE LV.

VALUES OF THE IONIZATION FUNCTION K' FOR STRONG ELECTROLYTES IN WATER AT HIGHER TEMPERATURES.

Potassium Chloride.

$C \times 10^3$	0.5	2.0	10.	80.	Temp.
$K' \times 10^2$	2.68	5.67	18.9	39.6	156°
	—	0.882	—	13.0	306°

Nitric Acid.

$C \times 10^3$	0.5	2.0	10.	80.	Temp.
$K' \times 10^2$	2.68	4.87	10.7	28.0	156°
	1.57	3.53	8.30	21.6	218°
	0.60	1.22	2.96	8.53	306°

Allowance must, of course, be made for the more or less continuous increase in the probable error of the conductance values as the temperature rises. The uncertainty in the value of the ionization function K', however, probably does not increase in the same proportion, since, at a given concentration the ionization of the salt decreases with temperature, and a given percentage error in Λ or Λ_0 has as a consequence a smaller percentage error in the value of K'. At the higher concentrations, at any rate, the values of K' are approximately correct. In the case of potassium chloride at 156°, the general course of the curve is similar to that of potassium chloride at 18°, but the value of the function is somewhat lower. At 306°, the value of the function K' is markedly lower than at 156°. Thus, at 0.08 normal, between 156° and 306°, K' changes from 0.396 to 0.13. Correspondingly, at lower concentrations the value of the function K' becomes much smaller. The change in the value of the function K' is most marked in the case of nitric acid. For this electrolyte, between 156° and 306°, the value of K' decreases approximately in the ratio of 1 to 4. For hydrochloric acid the change in the value of K' is much smaller than it is for nitric acid. Since, at 306°, the ionization curve of hydrochloric acid differs but little from that of potassium chloride, it is obvious that the value of the function K' for hydrochloric acid is approximately the same as for potassium chloride at that temperature. At 18° and 0.1 N, the value of K' is 0.5 for potas-

sium chloride and 1.1 for nitric acid. It is evident that at the higher temperatures the strong acids and bases are relatively much weaker than at lower temperatures.

Owing to uncertainties in the conductance values and the meagreness of the experimental material at the higher temperatures, it is not possible to determine whether or not the mass-action law actually is approached as a limiting form in the case of aqueous solutions; but it seems not unlikely that such is the case. In view of the high value of the ionization constant of water and the relatively low value of the ionization function of the acids and bases at higher temperatures, it follows that at these temperatures typical salts will be hydrolyzed to an appreciable extent in dilute solutions and that salts of slightly weaker acids and bases, and particularly of the polybasic acids and the polyacid bases, undergo appreciable hydrolysis.

3. *The Conductance of Solutions in Non-Aqueous Solvents as a Function of the Temperature.* In aqueous solutions, the maxima of the temperature-conductance curves lie at temperatures which are the lower the higher the concentration of the solution. The observed conductance change with rising temperature is the resultant effect of an increase in conductance due to increasing fluidity of the solvent, and a decrease, due to decreasing ionization of the salt. In very dilute solutions, where the ionization is approaching unity in all cases, the conductance increases with the temperature at all temperatures, since the ionization remains practically fixed in the neighborhood of unity, while the fluidity of the solvent increases. At higher concentrations, the ionization decreases with the temperature and presumably, at sufficiently high temperatures, it decreases at a sufficient rate to overcome the increase in conductance due to the fluidity change of the solvent. When the two effects balance, the temperature coefficient becomes zero, while at higher concentrations the temperature coefficient becomes negative.

In non-aqueous solutions, particularly in solvents of low dielectric constant, the temperature-conductance curves, as functions of the concentration, have a somewhat different form. In very dilute solutions, where the ionization is great, the conductance increases with the temperature because of the increasing fluidity of the solvent. At certain intermediate concentrations and above certain temperatures, the conductance decreases with the temperature, although at much lower temperatures the curve in general passes through a maximum. At much higher concentrations, that is, in the neighborhood of normal and above, the temperature coefficient is again throughout positive; that is, the conductance increases with the temperature at all temperatures. In the

following table are given values of the conductance of potassium iodide and ammonium sulphocyanate in SO_2 at temperatures from —33° to + 10°.[12]

TABLE LVI.

CONDUCTANCE OF ELECTROLYTES IN SO_2 AT DIFFERENT TEMPERATURES.

V	—33°	—20°	—10°	0°	+ 10°
		Potassium Iodide.			
1.00	37.7	44.1	46.9	51.2	54.5
128.0	65.9	66.9	66.5	64.5	62.0
4000.	139.0	151.0	162.5	166.3	168.7
		Ammonium Sulphocyanate.			
1.28	9.42	10.17	10.82	11.13	11.33
167.1	17.01	16.44	15.92	15.10	14.01

It will be observed that in the neighborhood of normal the conductance curve for both salts rises throughout with increasing temperature. In the neighborhood of 0.01 normal there is a slight increase between —33° and —20° in the case of potassium iodide, after which the conductance decreases throughout with the temperature. At the lower concentration, the conductance of ammonium sulphocyanate decreases throughout with increasing temperature. At a dilution of four thousand liters, the conductance of potassium iodide increases throughout with increasing temperature.

The effect of temperature on the conductance of solutions in non-aqueous solvents is readily interpreted in terms of Equation 11. What we have to consider is the influence of temperature upon the constants of this equation. We have seen that as the dielectric constant of the solvent decreases, *i.e.*, as the temperature rises, the value of the constant K decreases and ultimately reaches very low values. On the other hand, as the dielectric constant decreases, the exponent m increases while the constant D remains practically independent of the dielectric constant of the solvent. If the mass-action constant K is not too small, then, at high dilutions, the ionization of the electrolyte will approach unity, whatever the dielectric constant of the solvent. It follows, therefore, that with increasing temperature the conductance of such dilute solutions will increase throughout as the temperature increases. The constant D, as we have seen, determines the value of the ionization at very high concentrations. At unit ion concentration the value of the ionization is

[12] Franklin, *J. Phys. Chem.* *15*, 675 (1911).

$\gamma' = \frac{D}{1+D}$. For strong electrolytes D has a value in the neighborhood of 0.35. The ionization at this concentration is therefore 0.26 and the concentration of the salt at this ion concentration is accordingly in the neighborhood of 4.0 normal. If the constant D is independent of temperature, then the ionization at this concentration will remain fixed and consequently, with increasing temperature, the conductance of the solution will increase throughout, since the fluidity of the solution increases with increasing temperature. At very high and at very low concentrations, therefore, the conductance of all solutions should increase with increasing temperature. At intermediate concentrations, the ionization decreases as the dielectric constant decreases; that is, as the temperature increases. The decrease in the ionization in this region is largely determined by the decrease in the value of the constant K and increase in the value of the exponent m. For higher values of the dielectric constant and for salts having a high value of the constant K and low value of the constant D and a value of the exponent m less than 1, the change of the constants m and K has relatively a small effect upon the value of the ionization at intermediate concentrations. As a result, at low temperatures, or rather, for values of the dielectric constant greater than about 20, the ionization changes but little as the temperature increases and such solutions exhibit a positive temperature coefficient over the entire range of concentration. When, however, the dielectric constant falls below a value in the neighborhood of 20, the exponent m increases markedly and the constant K decreases largely with temperature. Consequently, at intermediate concentrations, the decrease in the ionization more than compensates for the increase in the conductance due to the increased fluidity of the solutions. The conductance of solutions at such intermediate concentrations, therefore, decreases with increasing temperature.

In order to illustrate the effect of temperature upon the conductance of solutions, ionization and conductance curves have been calculated for an electrolyte having the constants given in the following table:

TABLE LVII.

ASSUMED CONSTANTS OF EQUATION 11 TO ILLUSTRATE THE EFFECT OF TEMPERATURE ON CONDUCTANCE.

t	Λ_0	$K \times 10^4$	m	D
+10°	240	5.2	1.21	0.4
−10°	200	8.5	1.14	0.4
−30°	160	13.0	1.05	0.4
−50°	120	20.0	0.95	0.4

These constants correspond very nearly with those for solutions of potassium iodide in sulphur dioxide. The data for these solutions present certain inconsistencies, particularly at low concentrations, which render it very difficult to determine the precise values of Λ_0. Accordingly, the approximate constants given above have been adopted for the purpose of illustrating the effect of temperature upon the ionization and conductance of an electrolyte. The constant D is assumed to be independent of temperature. This condition is approximately fulfilled in solvents having dielectric constants lower than 25. The lower curves

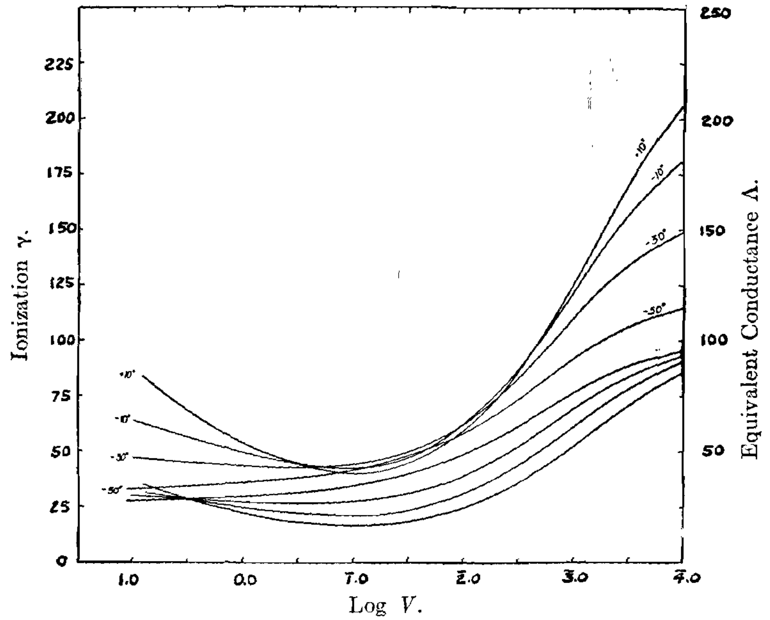

FIG. 33. Illustrating the Influence of Temperature on the Ionization and the Conductance of Electrolytes in Solvents of Relatively Low Dielectric Constant.

in Figure 33 represent the values of the ionization at different temperatures, the lower curves corresponding to the higher temperatures. In order to secure a plot on which the ionization and conductance values may be conveniently represented at all concentrations, the logarithms of the concentrations, instead of the concentrations themselves, have been plotted as abscissas. It will be observed that the ionization curves intersect at a concentration of 3.6 normal, corresponding to the value log C = 0.556. Actually, the intersections do not occur at a point, since the ionization is given by the equation $\gamma = \frac{D + K}{1 + D + K}$ and the constant K

decreases slightly as the temperature increases. The value of K, however, is so small that this effect is scarcely appreciable. At concentrations greater than 3.6 normal, the ionization increases with the temperature, and this increase is the greater the greater the value of m. In general, the increased conductance due to increased ionization in these regions is masked by the rapidly increasing effects of viscosity. In the neighborhood of normal concentration the viscosity effect becomes sufficiently great to overbalance the conductance increase due to increased ionization and the conductance-temperature curves pass through a maximum in this region, after which they fall off very rapidly. Nevertheless, it is to be noted that, in all cases for which measurements are available at different temperatures in very concentrated solutions, the conductance increases markedly with the temperature and this increase is the greater the higher the concentration. In Table LVIII are given values of the conductance of concentrated solutions of different salts in methylamine and ethylamine at a series of temperatures.[13]

What is striking in these results is the high value of the temperature coefficient at high concentration, as, for example, in solutions of silver nitrate in methylamine at $V = 0.2456$. Between $-33.5°$ and $-15°$ the conductance increases 91 per cent or 4.92 per cent per degree. The same holds true for solutions of silver nitrate in ethylamine, where the conductance increases nearly 100 per cent between $-33.5°$ and $-15°$ at 0.4083 N, while, between $-15°$ and $0°$, the conductance of solutions of ethylammonium chloride increases 6.76 per cent per degree at 0.17 N. It is true that the viscosity in these concentrated solutions must differ greatly from that of the solvent and the viscosity may change much more rapidly with the temperature in the case of the concentrated solutions than in that of the more dilute solutions. Nevertheless, it appears not improbable that the high value of the temperature coefficients of concentrated solutions is in part due to the increased ionization at these high concentrations.

As the concentration decreases below 3.6 N, the ionization decreases with increasing temperature. Those solutions for which m is less than unity exhibit an increase in ionization throughout with decreasing concentration, while those solutions for which m is greater than unity exhibit first a decrease and then an increase, so that the ionization curves pass through minima in the neighborhood of 0.1 N. These minima are the more pronounced the greater the value of m. In very dilute solutions, again, the ionization curves approach one another, corresponding to the fact that at low concentrations the ionization in all cases approaches unity.

[13] Fitzgerald, *J. Phys. Chem.* *16*, 621 (1912).

TABLE LVIII.

CONDUCTANCE OF CONCENTRATED SOLUTIONS IN METHYLAMINE AND ETHYLAMINE.

Methylamine.

Salt	V	—33.5°	—15°	0°	+15°
$AgNO_3$	0.2456	3.237	6.180	9.262	13.05
"	0.4790	14.33	20.56	25.67	30.8
"	0.9348	22.61	28.92	34.15	38.77
"	2.084	24.32	29.48	32.97	34.95
"	5.449	21.80	25.18	26.81	27.41
"	10.63	20.04	22.19	22.74	22.19
KI	0.6094	31.12	38.17	42.90	46.49
"	1.190	32.97	38.52	41.74	43.96
"	2.320	28.49	31.45	33.90	33.39

Ethylamine.

Salt	V	—33.5°	—15°	0°	+15°
$AgNO_3$	0.4083	2.135	3.989	5.824	8.072
"	0.7968	5.310	7.753	10.09	12.11
"	0.9928	5.67	8.44	10.55	12.52
"	1.981	5.820	7.625	9.082	10.25
"	3.953	4.320	5.400	6.141	6.719
"	7.886	2.683	3.181	3.454	3.690
"	15.73	1.677	1.818	1.939	1.939
"	31.39	1.212	1.277	1.285	1.188
LiCl	0.4215	—	—	1.586	2.080
"	0.8224	—	2.001	2.447	2.661
"	1.604	1.279	1.763	1.911	1.835
"	3.131	0.8484	0.9915	0.976	0.8052
$C_2H_5NH_3Cl$	0.1666	—	0.7197	1.450	2.440
"	0.3253	2.293	3.851	5.242	6.616
"	0.6346	—	5.090	5.820	6.406
"	0.7676	3.692	4.675	5.294	5.630
"	1.497	2.606	2.921	2.992	2.886
"	2.922	1.285	1.261	1.181	1.064

If the values of the ionization given by the lower curves in the figure are multiplied by the corresponding Λ_0 values, the conductance curves shown in the upper part of the figure are obtained. At low concentrations, where the ionization decreases only little with rising temperature, the increased conductance, due to temperature rise, more than counterbalances the decreased conductance due to decreased ionization, and the conductance therefore increases with increasing temperature. In very concentrated solutions, also, the conductance increases with the temperature since the change in ionization here is relatively small. At

intermediate concentrations, however, where the change in ionization is large, the conductance-concentration curves at different temperatures intersect one another in a more or less complicated manner, indicating that the conductance-temperature curves in this region exhibit maxima.

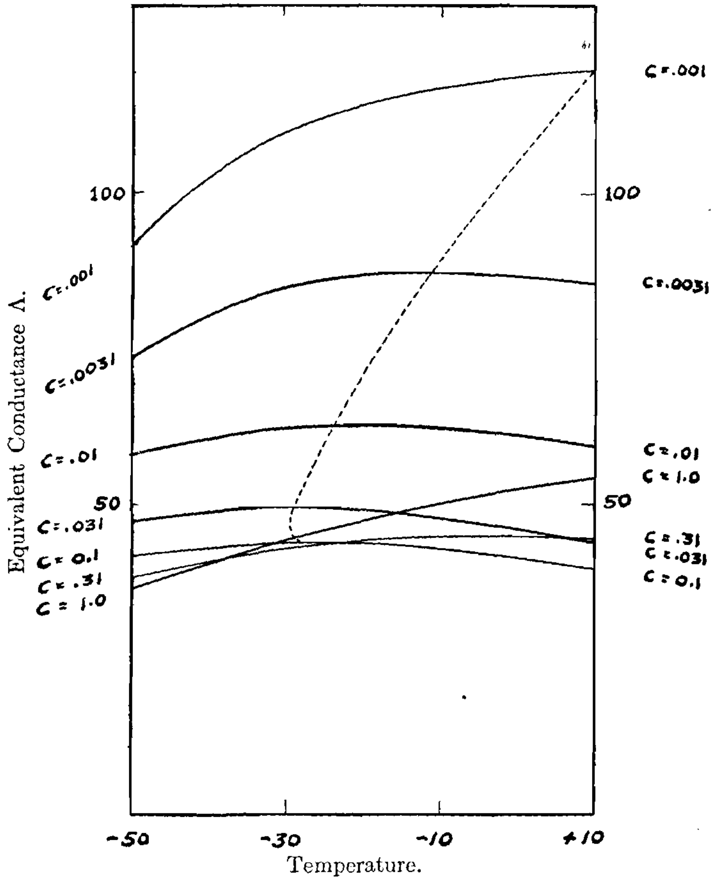

Fig. 34. Conductance-temperature Curves, illustrating the Relation between Conductance and Temperature for Solutions of Electrolytes at Different Concentrations in Solvents of Relatively Low Dielectric Constant.

The temperature-conductance curves are shown in Figure 34 for concentrations from 1.0 to 0.001 normal. At 0.001 normal the conductance increases throughout with increasing temperature. As the temperature rises, however, the conductance change due to a given temperature change becomes smaller and smaller and at this concentration the curve is very near a maximum at a temperature of $+10°$. At a concentration of 0.0031 normal, the conductance curve exhibits a very flat maximum at a

temperature of $-10°$. As the concentration of the solution increases, the maximum is shifted toward lower temperatures as indicated by the dotted curve. At 0.01 normal the maximum lies in the neighborhood of $-30°$, while at 0.031 normal the maximum is still further displaced in the same direction. At 0.1 normal the maximum remains at practically the same value, but at 0.31 normal the maximum is displaced toward higher temperatures, being very flat in this case and lying somewhere in the neighborhood of $-10°$. At 1 normal the maximum has arisen to temperatures above $+10°$ and the conductance increases markedly over the entire temperature range from $-50°$ to $+10°$. The maximum occurs at the lowest temperature at a concentration in the neighborhood of 0.1 N. These curves represent, in general, the behavior of solutions at different temperatures. They correspond very closely with the values obtained by Franklin[14] for solutions of KI in SO_2. The maximum in the conductance-temperature curves shifts from higher to lower temperatures with increasing concentrations, reaches a minimum, and thereafter again shifts from lower to higher temperatures with increasing concentration. In certain cases the effect of viscosity is such that it just counterbalances the effect of increased ionization over a considerable temperature interval. Ammonium sulphocyanate dissolved in sulphur dioxide is an example of this type, the conductance being practically independent of temperature at a concentration of approximately 0.1 normal. At concentrations greater than 0.1 normal the temperature coefficient of ammonium sulphocyanate solutions in sulphur dioxide is positive and is the greater the greater the concentration of the solution, while at lower concentrations the temperature coefficient is negative and initially increases with decreasing concentration. Ultimately, however, the sign of the coefficient must change. The fact that solutions in all solvents, without exception, exhibit maxima in the conductance-temperature curves at intermediate concentrations indicates that at the temperatures in question the constant m has reached a value near or greater than unity. Curves of this type have been observed in solutions in ammonia, sulphur dioxide, water, methyl and ethyl amine, and methyl and ethyl alcohols. It is not to be doubted that the phenomenon is a general one. That the temperature coefficient of solutions becomes positive at very high concentrations is indicated by practically all data available for solutions at high concentrations. In general, it has been found that the higher the concentration the greater the value of the temperature coefficient, or rather that the temperature coefficient passes through a minimum or negative value at intermediate concentrations.

[14] Franklin, *loc. cit.*

This result, however, does not become apparent in solutions of high dielectric constant, since the effects in question become marked only when the constant m approaches a value of unity or greater.

With increasing concentration, the temperature of the conductance maximum decreases, passes through a minimum and thereafter again increases in the more concentrated solutions. This course of the curve

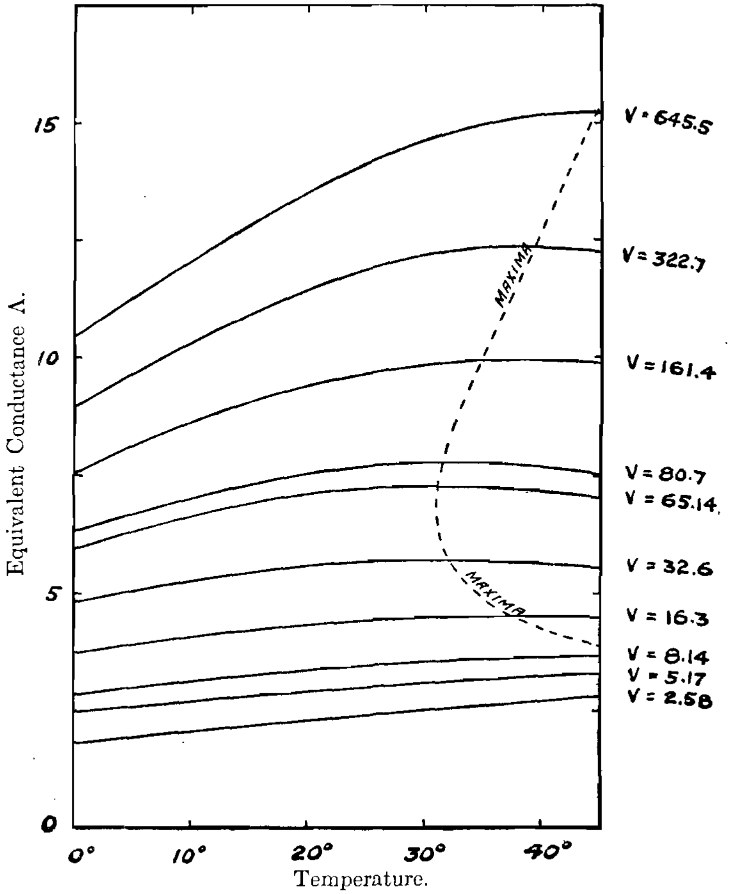

FIG. 35. Showing the Conductance as a Function of the Temperature for Solutions of Cobalt Chloride in Ethyl Alcohol at Different Concentrations.

is illustrated in Figure 35, in which are plotted the temperature-conductance curves for cobalt chloride, $CoCl_2$, in ethyl alcohol.[15] The course of the maximum is here indicated by the broken line. The lowest point of the maximum temperature is approximately 31° and at a dilution

[15] Rimbach and Weitzel, *Ztschr. f. phys. Chem.* 79, 279 (1912).

of approximately 50 liters. At higher concentrations the maximum temperature increases very rapidly, while at lower concentrations the maximum increases more slowly. In solvents of lower dielectric constant, the curve of maxima proceeds to lower temperatures. In Figure 36 are shown curves for cobalt chloride in acetone.[16] In this case the branch

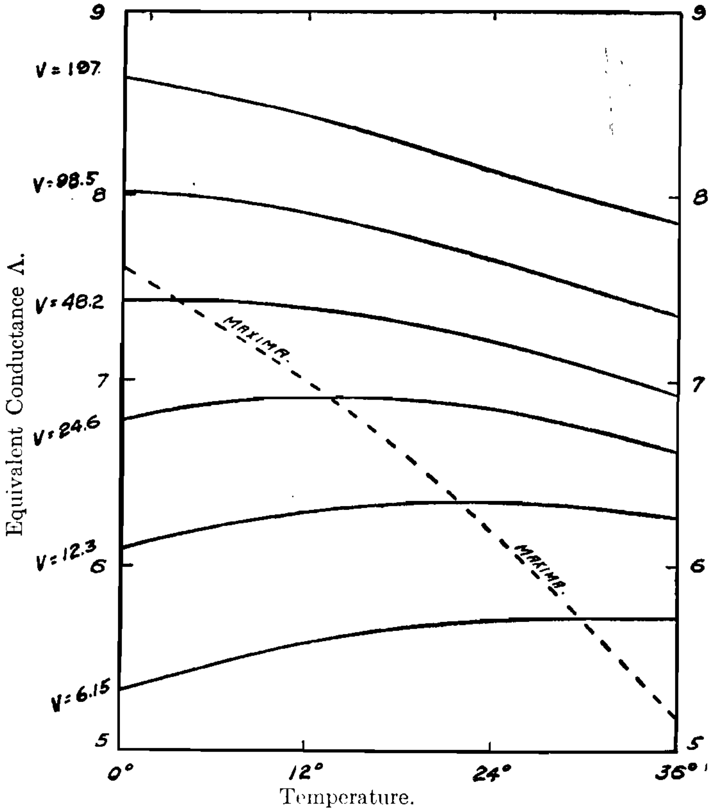

FIG. 36. Showing the Conductance as a Function of the Temperature for Solutions of Cobalt Chloride in Acetone at Different Concentrations.

of the maximum at lower concentrations lies at very low values of the concentration and does not appear on the figure. At higher concentrations the course of the maximum temperature is indicated by the broken line. At all points to the right of the maximum curve the temperature coefficients of the solution are negative. In Figure 37 are shown the conductance temperature curves for potassium iodide in methylamine, the dotted curves relating to dilutions greater than 28.2 liters.[17] The relation

[16] Rimbach and Weitzel, *loc. cit.*
[17] Fitzgerald, *loc. cit.*

among the curves in this case appears quite complex, since at the highest concentrations the conductance decreases with increasing concentration.

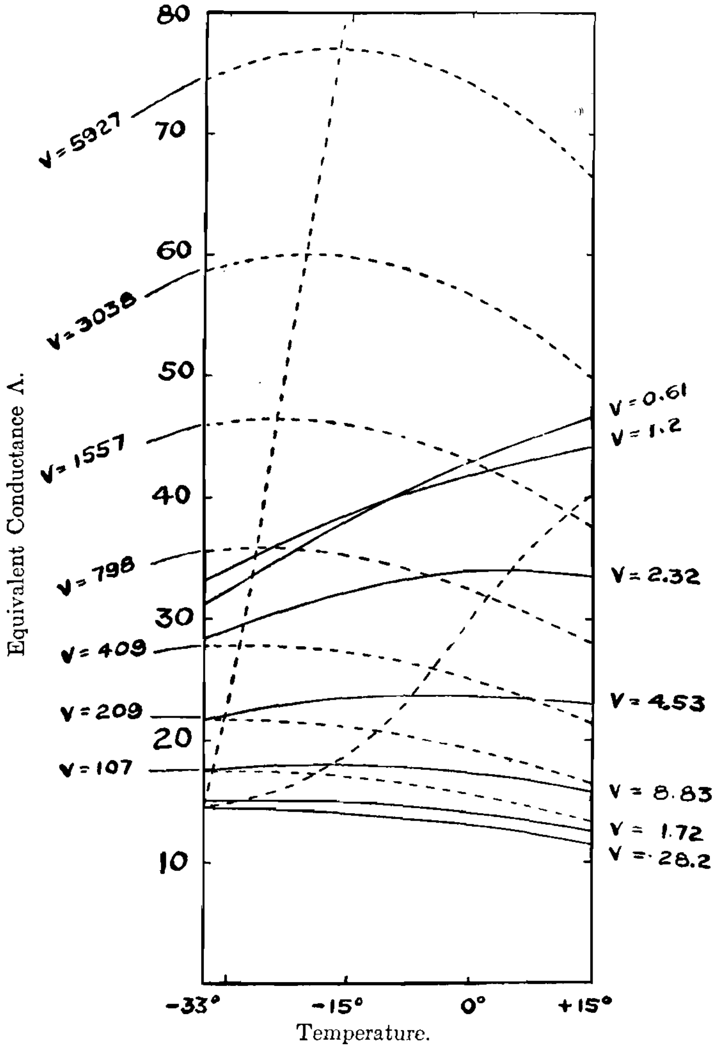

FIG. 37. Representing the Conductance as a Function of the Temperature for Solutions of Potassium Iodide in Methylamine at Different Concentrations.

The course of the maximum temperatures is indicated by the broken lines which meet at a point at a temperature of —33° and at a dilution of 28.2 liters. At higher concentrations the maximum proceeds to higher temperatures quite rapidly, while at lower concentrations the temperature

of the maximum increases slowly. Similar curves have been found for solutions in ethylamine, methylamine, and sulphur dioxide.

While the complete conductance-temperature diagram is not known for most solvents, sufficient data exist to indicate that it is a general property of electrolytic solutions to exhibit an increasing positive temperature coefficient at high concentrations. In certain cases this coefficient may be very great. In other cases the coefficient at lower concentrations is negative, decreasing with the concentration and becoming positive at higher concentrations. In the following table is given a list of temperature coefficients for substances dissolved in the liquid halogen acids.[18] The coefficients are positive unless otherwise indicated.

TABLE LIX.

TEMPERATURE COEFFICIENT $\alpha \times 100$ OF SOLUTIONS OF ELECTROLYTES IN DIFFERENT SOLVENTS.

Electrolyte	V_1	α_1	V_2	α_2	V_3	α_3
Hydrogen Bromide.						
Acetic Acid	4.30	2.62	0.571	2.72		
Butyric Acid	4.18	2.68	0.817	3.70		
Iso-valeric Acid	4.37	2.45	0.729	3.96		
Benzoic Acid	8.82	0.53	2.38	0.72	1.14	0.89
Metatoluic Acid	5.85	0.15	1.83	0.93		
Hydroxybenzoic Acid	18.4	1.00	1.36	2.15		
Methyl Alcohol	1.75	2.5	1.25	4.2		
Metacresol	15.0	—7.71	1.00	+1.16		
Thymol	43.6	.47	7.34	0.00		
Alphanaphthol	51.6	2.26	18.0	0.30		
Hydrogen Chloride.						
Propionic Acid	11.8	2.15	2.5	2.91		
Butyric Acid	50.1	2.80	0.792	3.27		
Methyl Alcohol	2.91	1.21	1.06	2.68		
Ethyl Alcohol	4.66	3.9	0.591	4.0		
Butyl Alcohol	5.07	5.23	0.574	6.5		
Resorcin	137.0	—1.33	6.29	0.00	0.539	+1.3

With the exception of solutions of thymol and alphanaphthol in liquid hydrogen bromide, the positive temperature coefficients throughout increase with increasing concentration. For lack of more comprehensive experimental data regarding the temperature coefficient of the substances named, it is impossible to hazard a guess as to the reason for the decrease of the positive temperature coefficients in the case of the solutions of these two substances. Particularly notable is the high nega-

[18] Archibald, *Journal de Chimie Physique 11*, 741 (1913).

tive temperature coefficient of the solution of metacresol in liquid hydrogen bromide at a dilution of 15 liters. Evidently, the temperature coefficient in this case changes greatly with the concentration since at normal concentration the coefficient is positive and equal to 1.16 per cent.

It is difficult to account for the large value of the positive temperature coefficients of the very concentrated solutions, except on the assumption that the ionization in the case of these solutions is relatively independent of the temperature. While the concentration at which this condition is fulfilled varies considerably with the nature of the dissolved electrolyte, it varies but little with the nature of the solvent. While at lower concentrations the ionization decreases throughout with the temperature, at higher concentrations the ionization increases with the temperature.

It is probable that, at very low concentrations, the temperature coefficient will always be found positive. The concentration at which this holds, however, may be very low indeed in the case of solvents of very low dielectric constant. It may be noted, in this connection, that the conductance-temperature coefficient of nearly all solvents is positive. It is true that, if no impurities were present, it might be expected that the ionization of the solvent would increase with the temperature. However, in most cases, the final conductance of highly purified solvents is due to impurities and not to the ionization of the pure solvent. Whatever these impurities may be, it is evident that they must be sufficiently ionized at these concentrations to yield a positive conductance-temperature coefficient.

The ionization as a function of the concentration at different temperatures is represented by a family of curves passing through two common points at a concentration zero, where the ionization is unity, and at a concentration corresponding to the ionization $\gamma = \frac{D}{1+D}$, which for solutions of potassium iodide in sulphur dioxide is in the neighborhood of 3.5 normal. At concentrations below this value the ionization decreases with the temperature. In very concentrated and very dilute solutions, the decrease in the ionization is comparatively small, and the conductance therefore increases with the temperature. At intermediate concentrations, the conductance at higher temperatures decreases with the temperature, while at low temperatures it increases with the temperature. If the Λ, T-curves are examined, it will be found that at intermediate concentrations the conductance curves exhibit a maximum. As the concentration decreases, however, this maximum is displaced toward higher temperatures and presumably would ultimately disappear at suf-

ficiently low concentrations. It is to be borne in mind, however, that at very high temperatures the value of the mass-action constant becomes extremely low, as may be seen from the value of this constant in the case of solvents having low dielectric constants. It is possible, therefore, that, in the case of solvents having relatively low dielectric constants, the mass-action constant has such a low value that a maximum in the conductance curves will not be observed in dilute solutions. At higher concentrations, again, the maximum is displaced toward higher temperatures and if it were possible to work with solutions of sufficiently high concentrations the maximum should disappear entirely. Data are not available in this case at temperatures approaching the critical point, but, in solutions in sulphur dioxide and ethyl amine, the conductivity increases with the temperature over those ranges of temperature for which conductance data exist.

The conductance of a given solution, therefore, appears to be a function, primarily, of the fluidity of the medium and of its dielectric constant. For a given type of salt the conductance curve in two solvents at different temperatures will be similar, provided that the two solvents have the same value of the dielectric constant.

4. *The Conductance of Solutions in the Neighborhood of the Critical Point.* Data relative to the ionization of solutions in the critical region are entirely lacking, for which reason it is not possible to interpret the results of conductance measurements with any degree of certainty. However, the conductance data indicate that the properties of solutions in the critical region do not differ materially from those of solutions at lower temperatures. Moreover, it appears that the property of forming electrolytic solutions is by no means confined to the liquid state of matter. Fluids above the critical point yield electrolytic solutions and even the solvent vapors themselves, below the critical point, possess the power of dissolving electrolytes, forming solutions which conduct the current.

It has already been pointed out that, as the critical point is approached, the conductance of solutions in solvents of low dielectric constant approaches a very low value, and that the conductance-temperature curve if extrapolated would intersect the temperature axis at a temperature not far removed from the critical temperature. It is known, however, that, once the critical point has been reached, the conductance falls only very slowly with increasing temperature. It other words, the conductance-temperature curves exhibit a discontinuity in the immediate neighborhood of the critical point. As will be seen below, this behavior is what we should expect when conductance measurements are carried out in sealed tubes, where the total volume of liquid and vapor remains

constant. In the immediate neighborhood of the critical point, the density of the solvent decreases very rapidly with increasing temperature, whereas beyond the critical region the density of the solvent medium remains fixed. The rapid decrease in conductance immediately below the critical point is to be ascribed to the rapid decrease in the density of the solvent medium.

It is to be expected that the ionization and consequently the conductance of solutions in the critical region will be governed largely by the dielectric constant of the medium, and it may be inferred that those liquids, which under ordinary conditions exhibit a very high dielectric constant, will likewise exhibit a relatively high dielectric constant in the critical region. In the case of sulphur dioxide and ammonia the dielectric constant in the critical region is very low, whereas in the case of the lower alcohols and water a relatively larger value of this constant is to be expected. Water would be an ideal substance for the purpose of studying the properties of electrolytic solutions in the critical region, were it not for the difficulties attending conductance measurements in this solvent at high temperatures. These difficulties, however, disappear very largely in the case of the lower alcohols, although it is to be expected that the ionization in the critical region will be markedly lower in these solvents than in water.

In Table LX are given values of the specific conductance of solutions of potassium iodide in methyl alcohol at a series of temperatures up to 252°.[19] The critical point lies in the neighborhood of 240° C. The reduced conductance values given in the last column are derived by multiplying the specific conductance (second column) by the fraction of the total volume of the tube occupied by the liquid (third column). If the true critical phenomenon is to be observed, the tube must initially be filled with an amount of liquid such that when the critical point is reached the tube is just filled with liquid. Obviously, as the liquid expands, the concentration of the solution decreases, and the corrected values of the specific conductance therefore represent values of this quantity on the assumption that the specific conductance varies as a linear function of the concentration. This condition is probably not fulfilled, but nevertheless represents an approximation somewhat nearer the truth than the measured values of the specific conductance. Moreover, in the immediate neighborhood of the critical region, where the volume of the liquid is almost equal to the entire volume of the tube, the corrected value of the specific conductance corresponds very nearly with the true value. If these corrected values are plotted against the tem-

[19] Kraus, *Phys. Rev. 18,* 40 and 89 (1904).

perature, then a break in the conductance curve itself will not occur at the critical point. The results are shown graphically in Figure 38.

TABLE LX.

SPECIFIC CONDUCTANCE OF KI IN CH_3OH THROUGH THE CRITICAL REGION, AT 3.34×10^{-4} *N*.

Liquid.

t	$\mu \times 10^6$	V/V	$\mu V/V \times 10^6$
90.0	908.4	0.4324	392.8
102.0	1006.0	.4363	438.9
123.0	1098.0	.4451	488.2
138.2	1126.0	.4548	511.9
149.0	1139.0	.4674	532.3
159.0	1126.0	.4764	536.2
171.0	1076.0	.4853	522.5
183.8	1006.0	.4979	500.9
197.0	740.4	.5095	377.3
208.5	617.0	.5137	314.3
220.0	431.2	.5445	234.8
225.0	337.5	.5569	187.9
230.0	252.1	.5693	143.5
237.0	186.0	.6005	111.6
238.0	157.6	.6094	96.05
238.5	143.7	.6183	88.88
239.0	127.0	.6275	79.69
239.5	107.5	.6362	68.39
240.04	83.71	.6628	55.50
240.4	63.92	.7432	47.50
240.5	55.46	.8074	44.78
240.6	45.29	.9566	43.32
Crit.	42.65	1.000	42.65

Gas.

t	$\mu \times 10^6$	t	$\mu \times 10^6$
240.7	42.14	242.45	36.10
240.8	41.56	243.4	34.45
240.9	40.98	244.4	32.88
241.0	40.41	245.46	31.24
241.2	39.52	247.1	29.11
241.4	38.68	249.1	26.59
241.6	37.89	252.0	23.92
241.92	37.06		

It will be observed that the conductance passes through a maximum somewhere between 159° and 197°, probably not far from 175°. Thereafter the conductance decreases rapidly, particularly in the immediate

neighborhood of the critical point, which in this case is 240.6°. At the critical point the rapid decrease in conductance with the temperature ceases abruptly and thereafter there is only a moderate decrease as the temperature increases. Between 239.5° and 240.6° there is a conductance decrease of approximately 50 per cent for a temperature change of 1°, whereas between 240.6° and 252° there is a decrease of less than 50 per cent for a temperature change of approximately 12°. The sharp break in the tangent to the curve at the critical point is very noticeable.

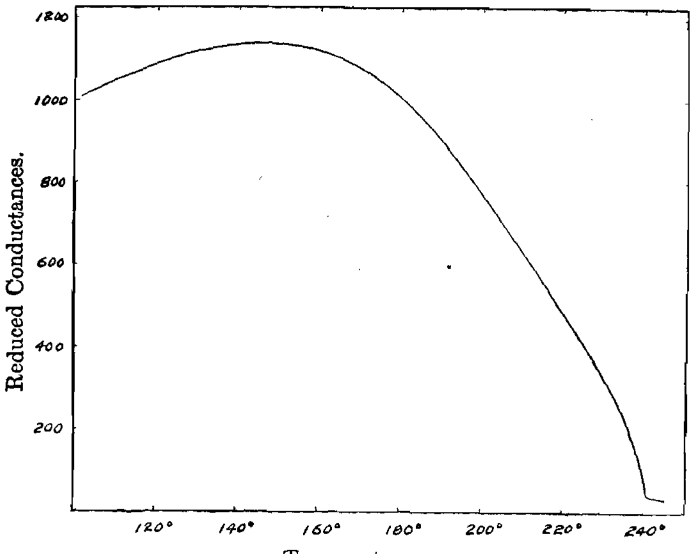

FIG. 38. Representing the Conductance of Solutions of Potassium Iodide in Methyl Alcohol as a Function of the Temperature through the Critical Region.

This result is obviously due to the fact that below the critical temperature the observed conductance change is due to the combined effect of temperature and of density change, while above the critical point it is due to temperature change alone.

As the critical point is approached, the salt becomes appreciably soluble in the vapor and is sufficiently ionized to render the vapor a fairly good conductor. In Table LXI, are given values of the specific conductance of liquid and vapor for solutions of ammonium chloride in methyl alcohol, together with the relative volume of the liquid phase $\frac{V_t}{V}$.

In this solution the amount of liquid in the tube was such that its mean density was below the critical density. In such case the true critical phenomenon does not occur since, if carried out under strictly equilibrium conditions, the liquid disappears at the bottom of the tube. In general, however, unless the amount of liquid is comparatively small,

TABLE LXI.

CONDUCTANCE OF 0.2245 PER CENT NH_4Cl IN CH_3OH IN THE CRITICAL REGION.

Temp.	μ Liquid	μ Vapor	V_l/V
234.0	1524.0	——	.4411
236.9	1236.0	1.574	.4333
239.0	930.3	2.177	.4261
240.0	760.0	3.568	.4147
241.0	605.7	6.381	.4000
241.9	469.7	14.64	.3707
242.5	257.7	38.66	.2806
→ Crit. Pt.			
243.1	67.25		
245.2	54.36		
247.1	47.62		
249.0	41.33		
254.0	30.19		

and is thoroughly stirred, it will be found that the meniscus fades away at some point above the bottom of the tube at a temperature corresponding to the critical temperature. At this temperature, the specific conductance of the vapor phase was approximately one sixth that of the liquid phase. The conductance of the vapor phase is readily appreciable as much as 5° below the critical point. Above the critical point the conductance of the solution in a gas below its critical density decreases with the temperature, the decrease amounting to something over 50 per cent for a temperature change of approximately 12°. In the immediate neighborhood of the critical point the conductance appears to change somewhat more rapidly than at higher temperatures.

The conductance of the vapor phase increases very rapidly with the temperature, and the more rapidly the nearer the temperature lies to the critical point. It is evident that several factors are here coming into play. In the first place, the concentration of the salt in the vapor phase increases with rising temperature; and, in the second place, the density of the vapor increases with increasing temperature. As follows from the results given below for the conductance of the fluid phase above the critical temperature as a function of the concentration of the solvent, the

conductance increases very rapidly with increasing density of the solvent phase. As the density of the vapor increases as the critical point is approached, the conductance is increased very largely because of the increase in the density of the vapor. The relations between the curves are shown in Figure 39.

In the following table are given values of the specific conductance of a 0.00463 normal solution of potassium iodide in methyl alcohol for different concentrations of the solvent.[20]

TABLE LXII.

CONDUCTANCE OF POTASSIUM IODIDE IN METHYL ALCOHOL ABOVE THE CRITICAL POINT FOR DIFFERENT DENSITIES OF SOLVENT.

$C = 0.1188\%$ $V = 0.3981$ $W = 0.1163$ $C = 0.00463\ N$

			$\mu \times 10^6$			
t	$W = 0.1163$	0.1023	0.0968	0.0815	0.0758	0.0588
239.0	—	—	—	—	—	1.892
241.0	—	—	—	—	—	1.736
241.3	—	—	—	—	4.783	—
241.32	—	42.24	—	—	—	—
241.5	56.41	—	—	—	—	—
241.6	—	—	28.80	—	—	—
241.7	—	—	—	16.56	—	—
242.0	53.95	36.35	26.54	10.90	4.468	—
242.9	—	—	—	—	—	1.662
243.0	50.54	32.48	24.23	9.36	4.141	—
244.0	47.90	30.59	22.47	8.626	3.884	—
244.9	—	—	—	—	—	1.521
245.0	—	28.80	21.25	7.886	3.656	—
245.1	45.51	—	—	—	—	—
247.0	41.68	25.79	19.14	7.081	3.247	—
247.2	—	—	—	—	—	1.387
250.1	36.97	22.04	16.90	6.003	2.824	1.230

In this table W represents the weight of solvent in the tube, V the total volume of the tube in cubic centimeters and C the concentration of the solution. The conductance curves are shown graphically in Figure 40. The density of the solvent in the different experiments, together with he conductance of the solutions at 245° and 250°, is given in Table LXIII. (See page 174.)

It is evident that the conductance of a solution containing a given amount of salt and a variable amount of solvent increases enormously as the density of the solvent increases. For an increase in the density of the methyl alcohol from 0.127 to 0.251, the conductance increases

[20] Kraus, *loc. cit.*

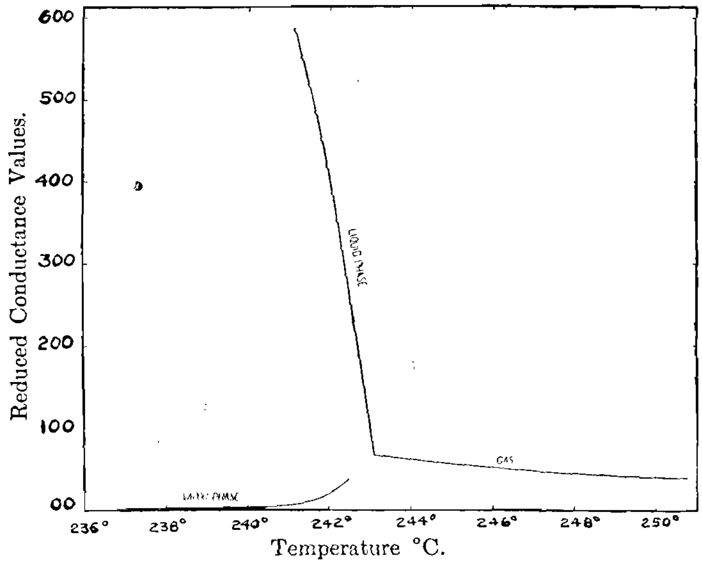

FIG. 39. Representing the Conductance of Ammonium Chloride in Methyl Alcohol as a Function of the Temperature in the Critical Region.

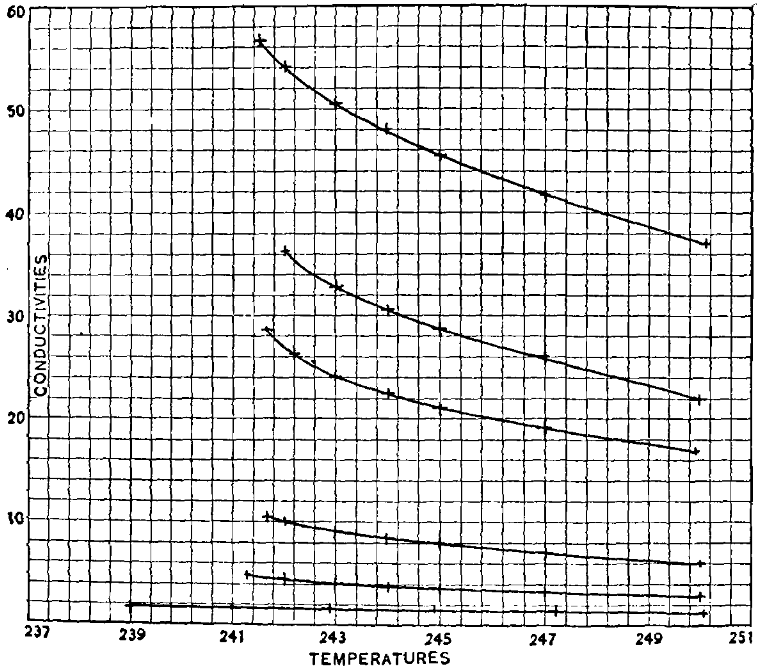

FIG. 40. Representing the Conductance of Potassium Iodide in Methyl Alcohol above the Critical Point at Various Concentrations of the Solvent.

TABLE LXIII.

CONDUCTANCE OF KI IN CH_3OH AS A FUNCTION OF THE DENSITY OF THE SOLVENT.

Density of Solvent	$\mu \times 10^6$ 245°	250°
0.251	45.6	37.2
0.220	28.8	22.6
0.208	21.2	16.83
0.178	8.0	6.0
0.163	3.7	2.8
0.127	1.44	1.2

from 1.44 to 45.6, or approximately 50 times. At 250° the increase in the conductance is not so great, since for the same concentration change the conductance increases only from 1.2 to 37.2, or 30 times. The Λ, t-curves indicate a fairly rapid decrease in the conductance immediately above the critical temperature. As the temperature rises these curves appear to approach a horizontal straight line. The lower the concentration, the less does the conductance change with the temperature.

At a given temperature, the addition of a given amount of solvent increases the conductance the more the greater the density of the solvent. In other words, the Λ,C-curves at constant temperature are strongly convex toward the axis of concentrations.

It is to be borne in mind that the conductance of a solution is a function of the number of carriers and the speed with which these carriers move. Unless the nature of the carriers changes very greatly, we should expect that the speed of the carriers would be the greater the lower the density of the solvent, since the viscosity of a gas increases with its density. Since, now, the conductance of a solution increases very rapidly with the density and since this increase is the greater the greater the density of the solvent, it is difficult to escape the conclusion that the increase in the conductance of these solutions is due to an increase in the number of carriers present in them.

According to the commonly accepted theory of electrolytic solutions, the change in the conductance of solutions as a function of the concentration is due to a change in the relative number of carriers; that is, to a change in the ionization of the electrolyte. Because of various difficulties which have arisen in accounting for the properties of strong electrolytes, some writers have suggested that strong electrolytes in solution are completely ionized. The study of the properties of nonaqueous solutions and of solutions at higher temperatures yields no apparent support for such an hypothesis. If the salts in solvents of low

dielectric constant are completely ionized, then it becomes exceedingly difficult to account, on the one hand, for the very low value of the conductance of these solutions at certain intermediate and low concentrations and, on the other hand, for the very rapid increase in the conductance of these solutions at higher concentrations. So, in the case of solutions in the neighborhood of the critical point, it is difficult to account for the rapid decrease in the conductance of the solution as the critical point is approached on the basis of this hypothesis. Again, in the case of solutions above the critical point, the large increase in the conductance of the solution as the concentration of the solvent increases is with difficulty accounted for on the assumption that the electrolyte is completely ionized, unless, at the same time, an hypothesis is introduced according to which the speed of the ions through the solvent medium is enormously increased by an increase in the concentration of the solvent. For such an hypothesis there is an entire lack both of experimental facts and of theoretical support.

On the other hand, if the fundamental elements of the usual theory of electrolytes are accepted, we are forced to the conclusion that the ionization of electrolytes is a complex function of the concentration and that, at very high concentrations, in the case of solvents of low dielectric constant, the ionization increases with the concentration. While theoretical support is lacking for this assumption, no theoretical principles are contradicted by such an hypothesis. Furthermore, if we assume that the ionization of electrolytes is a function of the concentration and is approximately measured by the conductance ratio $\frac{\Lambda}{\Lambda_0}$, the influence of temperature, of concentration, and of the viscosity of the solvent may be readily accounted for without contradicting known facts and without introducing any further hypotheses for which a theoretical foundation is lacking. In other words, on the basis of the ionization hypothesis, it is necessary to make only a single assumption whose correctness remains uncertain, whereas in the case of other hypotheses a number of assumptions are necessary. Unless other and more conclusive facts can be adduced in support of the hypothesis that the strong electrolytes are completely ionized in solution, this hypothesis is clearly untenable at the present time.

Chapter VII.

The Conductance of Electrolytes in Mixed Solvents.

1. *Factors Governing the Conductance of Electrolytes in Mixed Solvents.* Since the properties of electrolytic solutions are functions of the properties of the solvent, it follows that in the case of mixed solvents the properties will be functions of the concentration of the solvents in the mixture. We may have mixtures in which either one or both of the solvents are capable of forming electrolytic solutions with ordinary salts. In the case of water, mixtures are, as a rule, obtained only with other solvents which have the power of forming electrolytic solutions. In the case of certain non-aqueous solvents, however, mixtures may be obtained with solvents not capable of forming electrolytic solutions with ordinary salts.

The addition of a second solvent component to a solution of given concentration will in general affect the conductance in that the speed of the ions and the ionization of the electrolyte will be influenced by the addition of the second solvent. The conductance will therefore be a more or less complex function of the relative concentration of the two solvents. The effect of the addition of a second solvent will depend upon the concentration of the electrolyte as well as upon its nature.

In certain solutions, the formation of an electrolytic solution depends upon an interaction between the dissolved substance and the solvent. When such is the case, the conductance of the solution is often greatly affected by the addition of a second solvent component. Such is the case with solutions of the acids in non-aqueous solvents on the addition of water. The addition of a small amount of water to a solution of an acid in an alcohol, for example, has an enormous influence upon the properties of the resulting solution. Similar results are obtained in non-aqueous solutions of salts which exhibit a pronounced tendency to form hydrates, as, for example, calcium chloride.

If we assume that the nature of the ions remains fixed and independent of the nature of the second solvent, then we should expect the speed of the ions to be a function of the viscosity of the medium. The viscosity of a mixture of two solvents varies continuously with the relative concentration of the solvents. The viscosity curves may exhibit either a minimum or a maximum or they may vary continuously between

the values of the two pure media as extremes. If the viscosity of the two solvents differs greatly, then in general the viscosity of a mixture will lie intermediate between that of the two pure components. If the two solvents have approximately the same viscosity and particularly if both solvents are associated liquids, the viscosity curve will as a rule exhibit a maximum. Cases in which the viscosity curve passes through a minimum are rather exceptional.

The viscosity of a mixture of two solvents will in all cases be of the same order of magnitude as that of the two components. If the nature of the ions remains fixed, therefore, the speed of the ions may be expected to vary approximately in proportion to the fluidity change.

In adding a second solvent to a solution of an electrolyte in another solvent, an interaction may take place between the electrolyte and the added solvent. In this case, the nature of the ions will change and with it, in general, their speed. In some instances, the change in the speed of the ions due to this cause is relatively large.

In general, it may be expected that the ionization of a salt in a mixture of two solvents, particularly in dilute solutions, will have a value intermediate between those of the same electrolyte in the pure solvents. For we have seen that the ionization of a salt is a function of the dielectric constant of the medium, and the dielectric constant of a mixture of two solvents is in general intermediate between those of the pure components. Here again, however, we have to take into account the interaction between the electrolyte and the components which form the solvent medium. If interaction takes place between the second solvent and the electrolyte, then a new complex is formed whose ionization may differ greatly from that of the same electrolyte in the first solvent and, in fact, all of whose chemical properties may differ greatly from those of the original electrolyte in the first solvent. A considerable number of examples of this type are found in aqueous solutions. When, for example, ammonia is added to a solution of a silver salt in water, a complex is formed between the silver ion and ammonia, which apparently has the composition $Ag(NH_3)_2^+$ and whose properties are distinct from those of the normal silver ion in water. So, we find that salts of this ion are much more soluble than those of the normal silver ion, particularly in the case of the halides. Similar complexes are formed in the case of many other salts dissolved in water in the presence of ammonia, as, for example, salts of copper, zinc, cobalt, nickel, etc. The distinctive properties of the complex affect all the characteristic properties of the resulting electrolytic solution. So the addition of ammonia to a solution of a silver or a copper salt in water decreases the viscosity of the solution, until all

the metal has been transformed to the complex. This behavior is due to the fact that the solutions of this complex possess a negative viscosity relative to that of pure water, while solutions of the original salt possess a positive viscosity with respect to pure water.

In non-aqueous solutions, we find similar relations; that is, interaction often takes place between the second solvent component and the electrolyte. Thus, the ionization of solutions of a large number of salts appears to be greatly affected by the addition of a small amount of water. This is particularly the case with electrolytes which exhibit a marked tendency to form complexes with water. If a salt, which exhibits a marked tendency to form hydrates, is dissolved in a medium, with which this salt has little tendency to form a solvate complex, then the salt will be relatively little ionized when dissolved in this solvent. On addition of water to such a solution, the salt apparently forms a complex with water, whose ionization in the original solvent is much greater than that of the anhydrous salt. Solutions of potassium chloride or iodide, for example, are highly ionized in acetone and their ionization, and consequently their conductance, is but little affected by the addition of water. On the other hand, lithium chloride, which shows a pronounced tendency to form complexes with water, is ionized to only a relatively slight degree in pure acetone. On the addition of water to a solution of a lithium salt in acetone, the conductance is greatly increased. Similar results have been obtained in the case of calcium chloride.

2. *Conductance of Salt Solutions on the Addition of Small Amounts of Water.* In Table LXIV are given values of the conductance of solu-

TABLE LXIV.

CONDUCTANCE OF SALTS IN ANHYDROUS PROPYL ALCOHOL AT 25°.[1]

NaI		$Ca(NO_3)_2$ Anhydrous	
$C \times 10^3$	Λ_{mol}	$C \times 10^3$	Λ_{mol}
0.0623	19.94	0.363	5.140
0.1581	19.36	0.792	3.834
0.3902	18.36	1.617	2.894
0.6591	17.72	3.326	2.184
1.498	16.30	5.908	1.798
2.310	15.40	7.247	1.688
5.890	13.23	14.320	1.258
13.26	11.28	24.930	0.976
27.77	9.815	43.290	0.772
53.40	8.400		

[1] Kraus and Bishop, *J. Am. Chem. Soc.* 43, 1568 (1921).

tions of calcium nitrate and sodium iodide in propyl alcohol. In the case of calcium nitrate the values given are the molecular conductances whose limit at low concentration should be approximately twice that of the equivalent conductance. It will be observed that while sodium iodide is highly ionized, calcium nitrate is ionized to only a relatively small extent.

At a concentration of approximately 10^{-3} molal, the ionization of calcium nitrate is less than 15 per cent, whereas at the same concentration sodium iodide is very largely ionized. If the equivalent conductances are plotted against the concentrations, the curve of sodium iodide approaches a limiting form asymptotically, whereas that of anhydrous calcium nitrate is convex toward the axis of concentrations, the increase in conductance being the greater the lower the concentration of the electrolyte.

The addition of 0.185 mols of water per liter to the calcium nitrate solution, whose concentration was 0.045 N, raised the conductance from 0.772 to 2.036, and an additional 0.346 mols raised the conductance to 2.991. It is evident, therefore, that the addition of water to a solution of anhydrous calcium nitrate in propyl alcohol causes a large increase in the ionization of the salt. This follows, since the viscosity of the solvent is not materially affected by the addition of small amounts of water. It is true that, if a complex is formed on the addition of water to a solution of calcium nitrate, the speed of the ion may be affected by the addition of water, but it seems likely that, if anything, the speed of the complex will be lower than that of the original ion. However this may be, it is very unlikely that the speed of the complex could vary greatly from that of the anhydrous ion and the resulting change in the conductance must therefore be due to a change in the ionization of the electrolyte as a result of the formation of a complex with water.

TABLE LXV.

CONDUCTANCE OF $Mg(NO_3)_2 . 6H_2O$ IN ANHYDROUS PROPYL ALCOHOL AND IN PROPYL ALCOHOL CONTAINING 0.7 PER CENT WATER AT 25°.

Anhydrous Solvent		Solvent + 0.7% Water	
$C \times 10^3$	$\Lambda_{mol.}$	$C \times 10^3$	Λ
0.394	12.422	.298	17.774
0.865	10.730	1.950	9.062
1.942	8.932	3.758	7.326
3.483	7.774	6.339	6.188
6.406	6.408	11.670	5.096
9.804	6.026	19.460	4.400
19.89	4.674	30.410	3.921
36.12	3.866	49.560	3.555

In Table LXV are given values for the conductance of magnesium nitrate hexahydrate in anhydrous propyl alcohol and in propyl alcohol containing 0.7 per cent of water.

The original salt having been hydrated, it is probable that the complex hydrate was to some extent present in the solution. Nevertheless, the value of the molecular conductance is of the same order of magnitude as that of anhydrous calcium nitrate in propyl alcohol and the conductance curve is of the same general form. On the addition of water, the conductance of the magnesium nitrate is markedly increased, particularly in the more dilute solutions. The curve for the conductance in the presence of water twice intersects the curve for the conductance in the anhydrous solvent. This effect may in part be due to a change in the speed of the ions, owing to the presence of water, and in part to a more or less complex equilibrium which must exist between the dissolved electrolyte and the water.

Those salts which have only a slight tendency to form stable complexes with water are, as a rule, ionized more highly in such solvents as acetone and the alcohols than are salts which exhibit a pronounced tendency to form stable complexes with water. Correspondingly, the addition of water to a solution of a salt, which has little tendency to form complexes with water, has very little influence upon its ionization. The effect is scarcely observable in solutions of such salts as potassium and sodium iodides. In the case of lithium chloride dissolved in ethyl alcohol there is a slight increase in the ionization upon the addition of water. In Table LXVI are given values for the conductance of solutions of lithium chloride in ethyl alcohol in the presence of water.[2] It is evident from an inspection of this table that the conductance of lithium chloride in ethyl alcohol is increased slightly upon the addition of water. The effect is somewhat more marked at higher concentration.

TABLE LXVI.

CONDUCTANCE OF LiCl IN C_2H_5OH IN THE PRESENCE OF WATER AT 25°.

	C_{H_2O} Mols per Liter				Dilution of Electrolyte
	0	1	2	10	V
Λ......	17.7	18.8	19.7	24.2	20
	31.8	32.2	32.8	33.1	640

[2] Goldschmidt, *Ztschr. f. phys. Chem.* 89, 138 (1914).

3. *The Conductance of the Acids in Mixtures of the Alcohols and Water.* In aqueous solutions, the acids and bases occupy a unique position in that their solutions possess properties which, as a rule, differentiate them sharply from solutions of typical salts. The acids and bases in water are the only electrolytes which apparently conform to the mass-action law in this solvent. Furthermore, the ionization of different acids and bases differs greatly, while that of salts of the same type is practically the same at all concentrations. So, also, the speed of the hydrogen and hydroxyl ions is much greater than that of the ordinary ions at ordinary temperatures. In the case of acids, at any rate, many facts indicate an interaction between acid and water whereby a complex positive ion is formed.

In Table LXVII are given conductance values for solutions of hydrochloric acid in methyl alcohol in the presence of varying amounts of water.[3]

TABLE LXVII.

CONDUCTANCE OF HYDROCHLORIC ACID IN METHYL ALCOHOL IN THE PRESENCE OF VARYING AMOUNTS OF WATER AT 25°.

	Mols of H_2O per Liter						Conc. of
	0	0.1	0.2	0.5	1.0	2.0	Electrolyte
Λ...	115.4	99.6	91.3	81.6	78.1	67.1	0.10
	171.9	141.7	129.3	120.8	116.7	97.8	0.0015625
Λ_0..	192.	157.	143.	135.	130.	107.	0.00

The effect of adding water to a solution of hydrochloric acid in methyl alcohol is to greatly decrease the conductance of the solution and this effect is relatively independent of the concentration of the solute. It appears, therefore, that the ionization of hydrochloric acid is not materially affected by the addition of water, but that the speed of the hydrogen ion is greatly reduced. It is true that on the addition of water to methyl alcohol the viscosity is increased, but the viscosity change due to the small amounts of water added in the case of these solutions is inconsiderable and cannot account for the large decrease in the conductance of these solutions. Apparently, therefore, the change in conductance is due to a slowing up of the hydrogen ion, since it is known that the chloride ion is normal in its behavior in mixtures of alcohol and water. The values given for the limiting value of the equivalent conductance are approximate, since the extrapolation function employed in determining these values is uncertain.

[3] Goldschmidt and Thuesen, *Ztschr. f. phys. Chem.* *81*, 32 (1913).

Apparently, when water is added to a solution of hydrochloric acid in methyl alcohol, a complex is formed with water which moves with a much lower speed than does the normal hydrogen ion in pure methyl alcohol. It will be noted that the speed of the normal hydrogen ion in methyl alcohol is exceptionally high. The Λ_0 values for typical salts in this solvent lie in the neighborhood of 100. The hydrogen ion must therefore move with a speed roughly three times that of the chloride or potassium ion.

Solutions of hydrochloric acid in ethyl alcohol exhibit a similar behavior on the addition of water.[4] Values of the equivalent conductance of hydrochloric acid in ethyl alcohol in the presence of varying amounts of water are given in Table LXVIII.

TABLE LXVIII.

CONDUCTANCE OF SOLUTIONS OF HYDROCHLORIC ACID IN ETHYL ALCOHOL IN THE PRESENCE OF WATER AT 25°.

	Mols of H_2O per Liter									
	0	0.028	0.05	0.1	0.2	0.5	1.0	2.0	3.0	Dilution
Λ.....	74.2	63.2	58.5	52.6	47.4	42.8	41.8	42.4	44.4	1280
	35.0	32.0	30.4	27.5	24.2	21.3	21.4	23.3	26.1	10
Λ_0....	89.4	75.1	69.3	62.0	56.0	50.5	48.5	48.2	49.5	∞

The conductance curve passes through a minimum for a solution containing approximately two mols of water per liter. This minimum is slightly affected by the concentration of the acid. At lower concentrations the minimum occurs at a slightly higher concentration of water. The shift in the minimum point, following a change in the concentration of the acid, may in part be due to a change in the viscosity of the solution due to the addition of acid. On the other hand, it is possible that the ionization of the salt is materially affected by the presence of water, particularly at the higher concentrations. It may be assumed, however, that at very low concentrations of acid, the ionization is not materially changed due to the addition of water. If this is true, and the acid is highly ionized, the Λ_0 values should follow a curve corresponding approximately to that of the most dilute solution. In other words, the Λ_0 values should pass through a minimum somewhere between 1 and 2 normal with respect to water, which has been found to be the case. This indicates that the addition of water results in an initial decrease in the speed of the ions up to a concentration of about 2 normal, and thereafter in an increase on further addition of water.

[4] Goldschmidt, *Ztschr. f. phys. Chem.* 89, 132 (1914).

This is further indicated by results at higher concentrations of water. In the following table are given values for the conductance of hydrochloric acid in mixtures of water and ethyl alcohol at 25° for larger amounts of water.[5]

TABLE LXIX.

CONDUCTANCE OF SOLUTIONS OF HYDROCHLORIC ACID IN ALCOHOL IN THE PRESENCE OF WATER AT 25°.

C_{H_2O}	Equivalent Conductances at Dilutions $V = 12$	$V = 48$	$V = \infty$
0.0	34.3	43.6	67.
6.83	37.2	43.0	51.
13.85	60.3	65.8	75.5
27.68	115.	121.	130.
41.57	207.	218.	230.5

The values for the pure solvent do not agree with those given in Table LXVIII. It is possible that the values in this case are low owing to the presence of traces of water.[6] However, it is evident that, in the presence of water at higher concentrations, the conductance increases with addition of water. This may be due, in part, to an increased ionization, but it appears probable that it is also in part due to an increase in the speed of the hydrogen ion. That a complex between water and the hydrogen ions is initially formed is likewise indicated by other properties of these solutions such as the catalytic effects due to the hydrogen ion.[7]

In the case of the weaker acids, on addition of water, the conductance curve is modified the more the weaker the acid. In Table LXX are given values for the conductance of sulphosalicylic acid in ethyl alcohol.[8] In solutions of sulphosalicylic acid, there is a marked decrease in the conductance on addition of small quantities of water up to normal concentration, but the effect is not as great as it is in solutions of hydrochloric acid.

TABLE LXX.

CONDUCTANCE OF SULPHOSALICYLIC ACID IN C_2H_5OH AT 25° IN THE PRESENCE OF WATER. $V = 160$.

C_{H_2O}	0	.003	.019	.1	.2	.5	1.0
Λ	49.0	49.0	45.4	37.0	32.8	29.9	29.5

[5] Kailan, *Ztschr. f. phys. Chem.* *89*, 678 (1914).
[6] Kailan, *loc. cit.*
[7] Goldschmidt and Thuesen, *loc. cit.*, p. 62.
[8] Goldschmidt, *Ztschr. f. phys. Chem.* *89*, 139 (1914).

In the following table are given values for the conductance of picric acid in methyl alcohol in the presence of water.[9]

TABLE LXXI.

CONDUCTANCE OF PICRIC ACID IN CH_3OH AT 25° IN THE PRESENCE OF WATER.

	Concentration of Water				Conc.
	0	.5	1.	2.	of Acid
Λ..........	9.32	12.7	16.3	23.4	0.1
	56.73	63.7	70.2	75.7	0.0015625

In this case, the conductance effect due to addition of water is the reverse of that in solutions of stronger acids. The conductance increases throughout as the concentration of water increases. It is evident that the ionization of picric acid is much smaller than that of the stronger acids. The increase in the conductance at the higher concentration is much more marked than it is at the lower concentration, indicating that at higher concentration, at least, an increase in the ionization due to the addition of water is a primary factor in causing an increase in the conductance of the solution. It may be presumed that the speed of the hydrogen ion is independent of the nature of the acid, and that consequently the Λ_0 values for picric acid decrease with increasing amounts of water, until fairly high concentrations are reached. In the following table are given approximate values of Λ_0 for picric acid dissolved in methyl alcohol in the presence of water.[10]

TABLE LXXII.

CHANGE OF Λ_0 FOR PICRIC ACID IN METHYL ALCOHOL WITH VARYING AMOUNTS OF WATER.

C_{H_2O}	0	.5	1.	2.
Λ	182	108	98	90

These values of Λ_0, while only approximate, nevertheless cannot differ greatly from the true values and clearly indicate that the increase in the conductance of picric acid is due to an increased ionization of the acid as a result of the presence of water.

In solutions of weaker acids, the effect of water on the ionization of the acid is even more pronounced. In the following table are given values for trichlorobutyric acid: [11]

[9] Goldschmidt and Thuesen, *loc. cit.*, p. 35
[10] *Ibid.*, *loc. cit.*
[11] *Ibid.*, *loc. cit.*, p. 37.

TABLE LXXIII.

CONDUCTANCE OF 0.2 N TRICHLOROBUTYRIC ACID IN CH_3OH IN THE PRESENCE OF WATER.

C_{H_2O}	0	1.0	2.0
Λ	0.446	0.825	1.283

In a 0.2 normal solution of this acid the conductance is increased 100 per cent on the addition of one mol of water. In other words, the ionization is increased somewhat over 100 per cent by this addition of water. In this respect the acids behave in a manner similar to that of typical salts which have a great tendency to form hydrates.

The effect of water on the ionization of the weaker acids is clearly shown in the increased value of the ionization constants of these acids on addition of water. In Table LXXIV are given values of the ionization constant[12] for trichloroacetic acid in absolute alcohol and in alcohol containing 0.622 mols of water at different dilutions. Excepting at the highest concentrations, the constant varies but little with the concentration of the acid.

TABLE LXXIV.

IONIZATION CONSTANT OF TRICHLOROACETIC ACID IN ALCOHOL IN THE ABSENCE AND IN THE PRESENCE OF WATER.

	$K \times 10^{-6}$	
V	Pure Alcohol	$C_{H_2O} = 0.622$ N
5.5	5.03	31.1
11.	4.74	29.3
22.	4.45	28.6
44.	4.45	27.6
88.	4.50	27.6
176.	—	28.4

It is evident that, due to the addition of 0.622 mols of water, the ionization constant of trichloroacetic acid is increased approximately six times. Corresponding to this increase in the value of the ionization constant of the acid, the conductance of the acid is obviously greatly increased. The effect of water on the conductance of different electrolytes is shown in Figure 41. The great percentage increase in the conductance of trichloroacetic acid will be noted in contrast to a smaller increase in the case of picric acid and lithium chloride and a large decrease in that of hydrochloric acid.

[12] Braune, *Ztschr. f. phys. Chem.* 85, 170 (1913).

It seems fairly clear that, on the addition of water to a solution of an acid in alcohol, a complex is formed between the acid and the added water. The hydrogen ion of this complex moves with a speed much lower than that of the normal hydrogen ion in alcohol or in pure water. In the case of the weaker acids, the ionization of the hydrated acid is

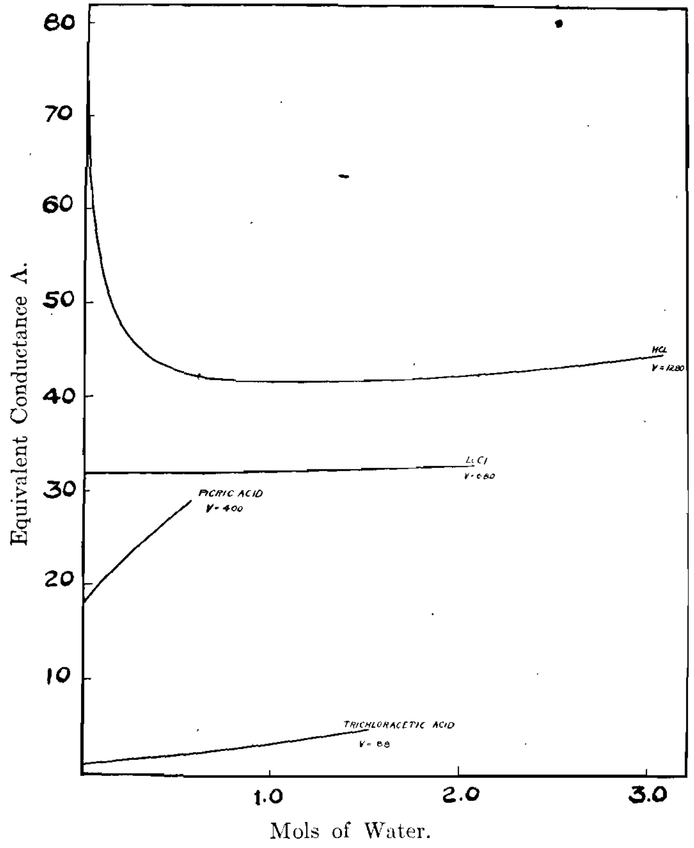

FIG. 41. Illustrating the Influence of Water on the Conductance of Different Electrolytes in Ethyl Alcohol.

much greater than that of the unhydrated acid. In solutions of salts in non-aqueous solvents, there is, as we have seen, a similar increase in ionization on the addition of water in the case of those salts which exhibit a pronounced tendency to form complexes with water. In these cases, therefore, the process of ionization is intimately connected with the formation of a more or less definite complex, and since these complexes are formed on the addition of a small amount of water to solutions in

anhydrous solvents, there is all the more reason for believing that these complexes exist when the salts are dissolved in pure water.

4. *Conductance in Mixed Solvents over Large Concentration Ranges.* A considerable number of systems have been studied in which salts have been dissolved in mixtures of two solvents miscible in all proportions. In these solutions the conductance has not been studied for small additions of either component. As a rule, the concentration was varied by intervals of 25 per cent. In such cases, the change in the viscosity of the medium, as well as that in the ionization of the electrolyte, makes itself felt.

When the two solvents have approximately the same dielectric constant and the dissolved salts are ionized to practically the same extent in the two solvents, then the conductance of solutions in mixtures of these solvents is determined primarily by the viscosity of the mixtures. In other cases, where the viscosity change is small and the ionization of the salt in the two solvents differs greatly, the form of the curve is largely dependent upon the ionization change brought about by the change in the composition of the mixture.

In Figure 42 are shown values of the fluidity of mixtures of acetone with water, methyl and ethyl alcohol at 0°.[13] In Figure 43 are shown fluidity curves for mixtures of methyl alcohol with water and ethyl alcohol,[14] and nitrobenzol with methyl and ethyl alcohols,[15] at 25°. The values are given in Table LXXV. In the case of these curves the precise

TABLE LXXV.

THE FLUIDITY OF MIXTURES AS A FUNCTION OF THEIR COMPOSITION.

Solvent		Per Cent B					
A	B	0	25	50	75	100	
H_2O	Acetone ...	56.24	34.12	33.03	58.80	244.1	$t = 0°$
CH_3OH	Acetone ...	122.2	153.9	187.4	222.2	244.1	
C_2H_5OH	Acetone ...	53.88	96.08	147.0	200.4	244.1	
H_2O	CH_3OH ...	112.3	76.18	67.72	83.6	144.4	$t = 25°$
H_2O	C_2H_5OH ..	112.3	55.22	41.56	47.21	87.4	
$C_6H_5NO_2$	CH_3OH ...	54.29	84.4	110.9	142.3	166.4	
$C_6H_5NO_2$	C_2H_5OH ..	54.3	73.3	82.7	88.2	87.4	
C_2H_5OH	CH_3OH ...	87.36	105.5	124.9	147.3	164.4	

values are represented only for the pure solvents and the mixtures having compositions of 25, 50 and 75 per cent, smooth curves having been

[13] Jones, Bingham and McMaster, *Ztschr. f. phys. Chem.* 57, 193 (1906).
[14] Jones and Veazey, Conductivity and Viscosity in Mixed Solvents, Carnegie Reports, p. 196 (1907).
[15] Jones and Veazey, *Ztschr. f. phys. Chem.* 62, 49 (1908).

drawn through these points. At intermediate concentrations the true curves may vary considerably from the curves as drawn, particularly at concentrations in the neighborhood of the axes. Nevertheless, the curves show in a general way the relation between the fluidity and the composition of these mixtures. The fluidity curves of all mixtures in which

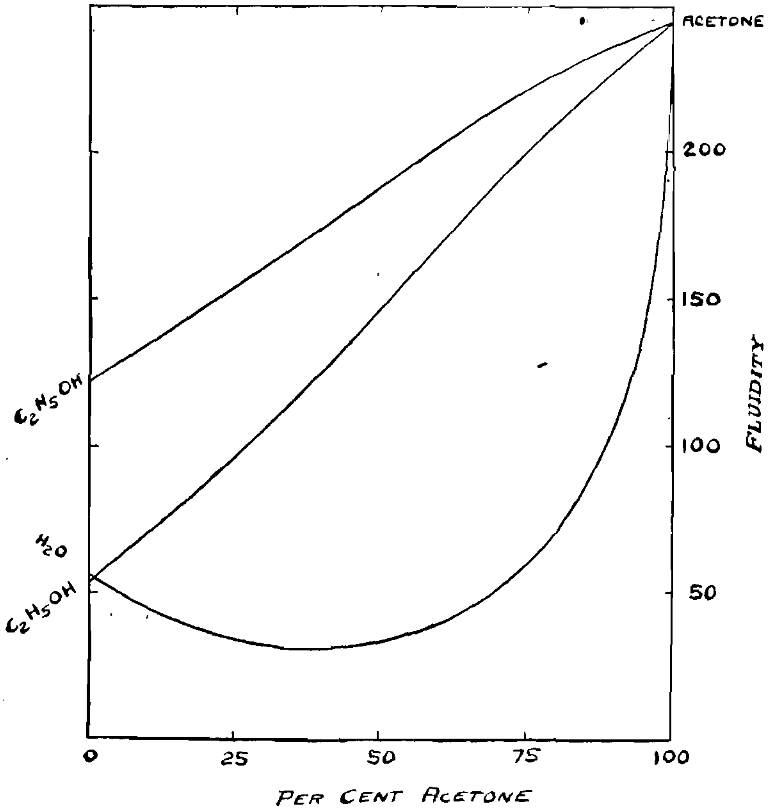

FIG. 42. Representing the Fluidity of Mixtures of Acetone with Various Solvents at 0° as a Function of Composition.

water is one component are characterized by a pronounced minimum, which lies roughly at a composition of 50 per cent. When the fluidity of the second solvent differs greatly from that of water, the minimum is displaced in the direction of the solvent having the lower fluidity. In mixtures of solvents of the same type, such as methyl and ethyl alcohols, as well as in mixtures of the alcohols and nitrobenzol, or the alcohols and acetone, the curves approach more or less closely to straight lines, the viscosity of the mixture being throughout intermediate between that of

the two components. When the two components have nearly the same fluidity, the fluidity curve exhibits a slight minimum.

It is apparent that the fluidities of mixtures in general differ considerably from those of the pure components and it is to be expected that the conductance of solutions in such mixtures will be materially affected by the viscosity change of the solvent. In those cases in which the elec-

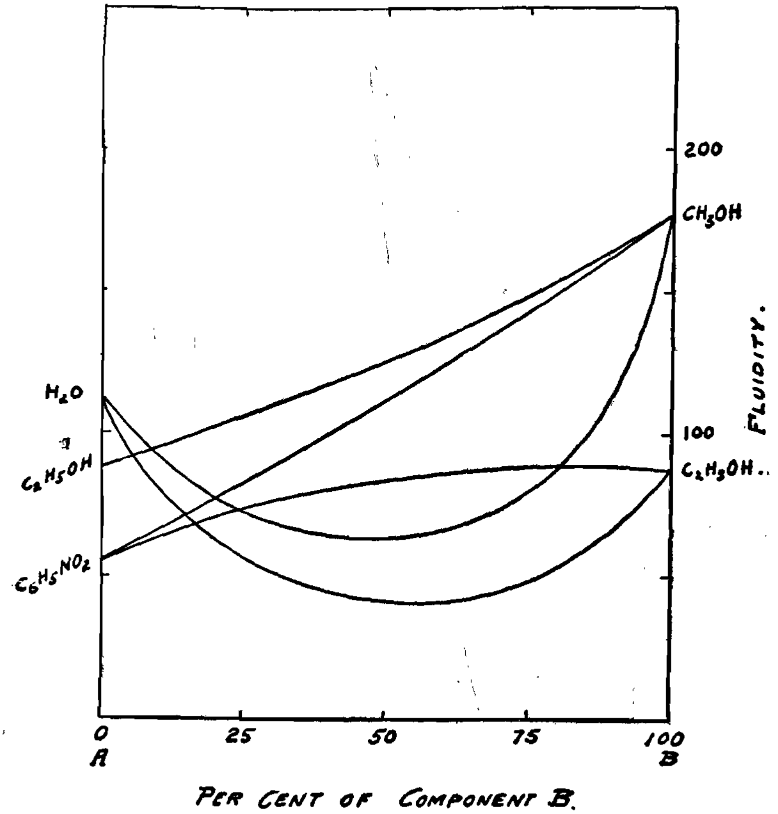

FIG. 43. Fluidity of Various Mixtures at 25°.

trolyte is largely ionized, it is to be expected that the conductance of a solution in a mixture of two solvents will vary approximately in accordance with the fluidity of the mixture. At higher concentrations a similar correspondence between the conductance and the fluidity is to be expected when the ionization of the electrolyte is the same in the two solvents. In general, this will be the case when we have solvents which have the same dielectric constant, and an electrolyte which does not exhibit a marked tendency to form solvates. In other cases, when the ionization is

largely dependent upon the formation of solvates between the electrolyte and one or the other of the solvent components, the ionization of the salt in the mixture, rather than the fluidity of the mixture, will determine the form of the conductance curve and this will be the more true, the more nearly the fluidity curves are linear functions of the composition.

In Figure 44 are shown conductance curves for solutions of tetraethylammonium iodide in mixtures of water[16] with methyl and with

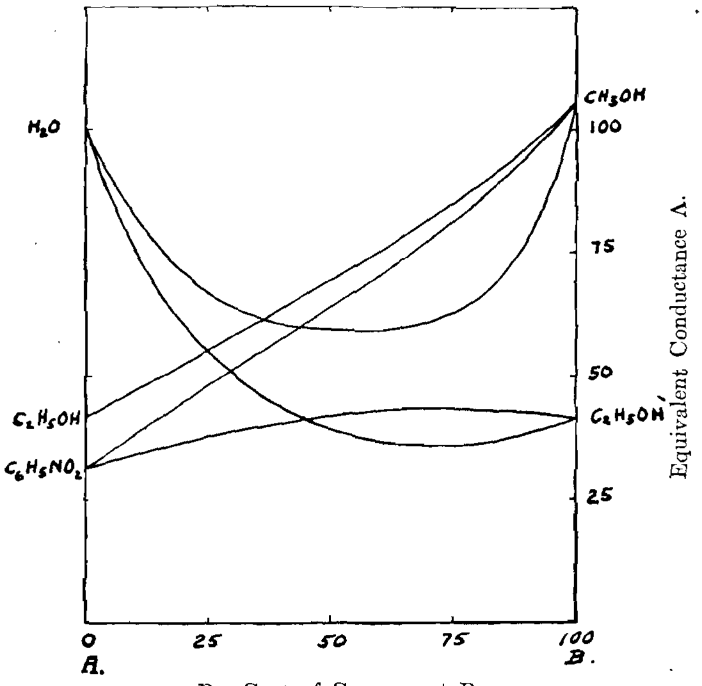

FIG. 44. Conductance of Tetraethylammonium Iodide in Solvent Mixtures at 25° at $V = 800$.

ethyl alcohol, nitrobenzol[17] with methyl and with ethyl alcohol, and methyl with ethyl alcohol.[16] The data from which the curves are drawn are given in Table LXXVI.

Comparing the conductance curves with the fluidity curves, it is clear that in these solutions of tetraethylammonium iodide there is a close correspondence between the two. The conductance curves for mixtures of methyl alcohol, ethyl alcohol and nitrobenzol correspond very closely with the fluidity curves. So, also, in mixtures of water with ethyl and

[16] Jones, Bingham and McMaster, *loc. cit.*, p. 257.
[17] Jones and Veazey, *loc. cit.*, p. 44.

TABLE LXXVI.

CONDUCTANCE OF TETRAETHYLAMMONIUM IODIDE IN MIXED SOLVENTS AT 25° AT A DILUTION OF 800 LITERS.

Solvent		Per Cent B				
A	B	0	25	50	75	100
H_2O	CH_3OH ...	100.6	67.03	55.17	62.50	105.3
H_2O	C_2H_5OH ...	100.6	54.53	38.68	35.51	41.46
$C_6H_5NO_2$	CH_3OH ...	31.44	47.91	63.54	80.53	105.3
$C_6H_5NO_2$	C_2H_5OH ...	31.34	37.88	41.87	43.51	41.46
C_2H_5OH	CH_3OH ...	41.46	55.20	69.44	84.22	105.3

methyl alcohols, a pronounced minimum is found in both conductance curves. Finally, in mixtures of nitrobenzol and ethyl alcohol, the conductance curve exhibits a slight maximum corresponding with the maximum in the fluidity curve. In general, salts which show little tendency to form stable complexes with water, in other words, those salts which exhibit a negative viscosity in aqueous solutions, yield conductance curves closely resembling those for tetraethylammonium iodide. It may be noted, however, that the conductance for tetraethylammonium iodide in methyl alcohol is abnormally high, being in fact somewhat greater than that of the same salt in water. In general, the conductance of salts in methyl alcohol is somewhat lower than that of salts in water, even though the viscosity of water is greater than that of methyl alcohol. The curves for solutions of other binary salts do not differ materially from those of tetraethylammonium iodide. In the case of electrolytes of this type, the ionization in a given solvent is near the maximum and is not appreciably affected by the addition of a small amount of another solvent. Moreover, the ionization of typical salts in these solvents does not differ greatly at concentrations approaching 10^{-3} normal. The form of the conductance curves, therefore, is determined primarily by the fluidity of the solvent mixtures.

TABLE LXXVII.

CONDUCTANCE OF SOLUTIONS OF POTASSIUM IODIDE IN MIXTURES OF ACETONE WITH METHYL AND ETHYL ALCOHOLS AND WATER AT 0°.

Per Cent Acetone ..	0	25	50	75	100	
H_2O	78.0	47.8	37.5	44.1	120.0	$V = 1600$
CH_3OH	71.7	83.9	94.1	106.5	120.0	$V = 1600$
C_2H_5OH	28.6	40.1	61.3	84.8	120.0	$V = 1600$
H_2O	76.7	44.6	36.3	41.6	100.4	$V = 200$
CH_3OH	65.7	74.1	82.7	93.1	100.4	$V = 200$
C_2H_5OH	22.0	35.5	52.2	72.0	100.4	$V = 200$

In Table LXXVII are given values for the conductance of potassium iodide at 0° in mixtures of acetone with methyl and ethyl alcohols and water [18] at the concentrations V = 1600 and V = 200. The results are shown graphically in Figure 45. It is apparent that in solutions of potassium iodide in mixtures containing acetone, the general form of the conductance curves corresponds with that of the fluidity curves. However, the deviations from the fluidity curves in these solutions are considerably

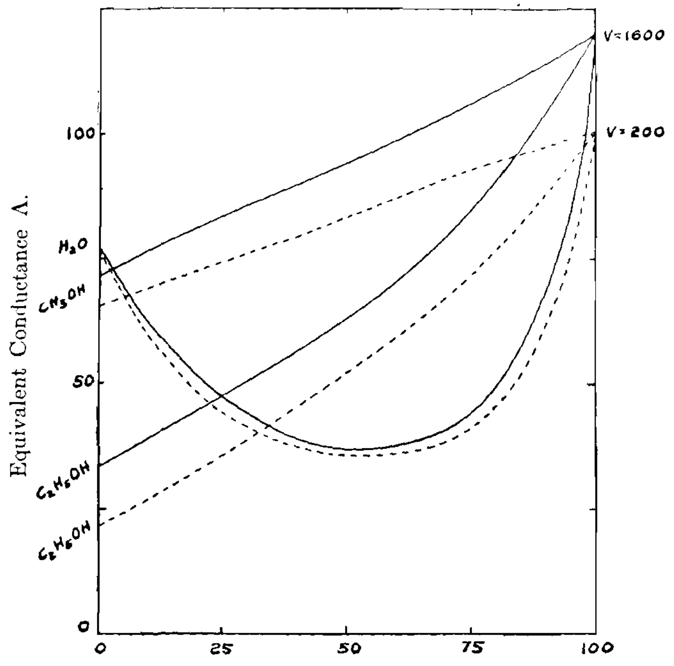

FIG. 45. Conductance of Potassium Iodide in Acetone Mixtures at 0° at Dilutions $V = 200$ and $V = 1600$.

greater than in solutions of tetraethylammonium iodide in mixtures of the alcohols and water. This is doubtless due to the relatively low ionizing power of acetone and its selective action upon different electrolytes, as well as upon the exceptionally high value of the fluidity of pure acetone with respect to that of the other solvents. The concentration change from a dilution of 1600 to 200 has only an immaterial influence upon the form of the curves.

The ionization of acetone solutions of salts which exhibit a marked tendency to form complexes with water, or other solvents, is very low. Under these conditions, the change in the ionization of the electrolyte due

[18] Jones, Bingham and McMaster, *loc. cit.*, p. 193.

to the addition of a second solvent becomes apparent. In Table LXXVIII are given values for the conductance of lithium bromide in mixtures of acetone with methyl and ethyl alcohols and water.[19]

TABLE LXXVIII.

THE CONDUCTANCE OF LITHIUM BROMIDE IN MIXTURES OF ACETONE WITH METHYL AND ETHYL ALCOHOLS AND WATER AT 0°.

Per Cent Acetone	0	25	50	75	100	
H_2O	56.12	35.71	28.34	31.65	70.89	$V = 1600$
CH_3OH	57.63	60.38	67.02	84.15	70.89	
C_2H_5OH	20.79	29.21	50.98	66.28	70.89	
H_2O	47.25	28.82	21.70	24.00	11.91	$V = 10$
CH_3OH	35.92	35.03	34.27	29.77	11.91	
C_2H_5OH	10.55	14.72	19.23	19.16	11.91	

The results are shown graphically in Figure 46. An examination of the curves shows a very complex behavior on the part of these solutions compared with that of solutions of potassium iodide in the same solvents. In mixtures of acetone and methyl alcohol, at the lower concentration,

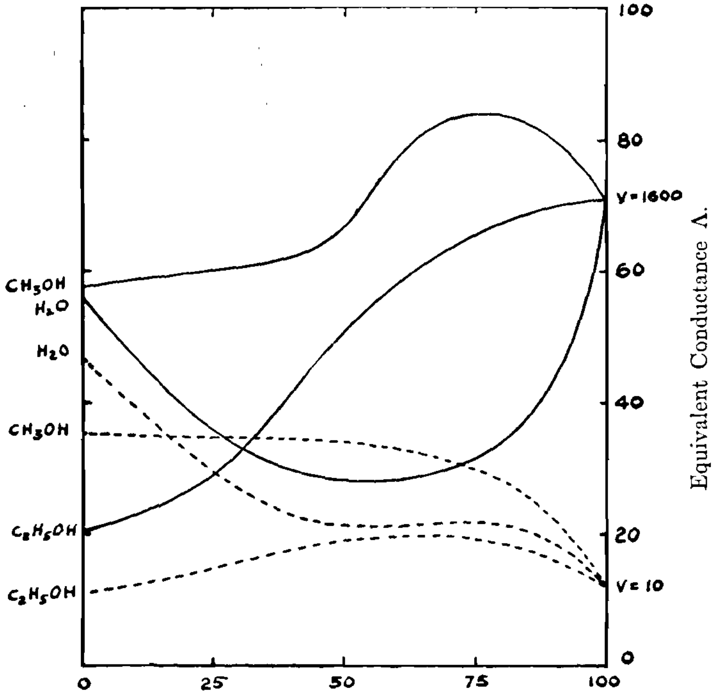

FIG. 46. Conductance of Lithium Bromide in Acetone Mixtures at 0° at $V = 10$ and $V = 1600$.

[19] Jones, Bingham and McMaster, *loc. cit.*, p. 257.

the conductance curve exhibits a pronounced maximum. The curve for ethyl alcohol mixtures exhibits a pronounced inflection point, while that for water merely exhibits a minimum corresponding to the minimum in the fluidity curve of the mixtures of acetone and water. At the higher concentration, the curve for water initially rises steeply to a very flat maximum and minimum, after which it rises with increasing concentration of water, the curve corresponding roughly to the fluidity curve of the mixtures within the region of these compositions. The conductance of solutions in mixtures of acetone and methyl alcohol rises sharply for initial additions of methyl alcohol, after which it remains practically constant until the axis of the pure methyl alcohol is reached. With ethyl alcohol the conductance likewise increases markedly for the initial additions. Thereafter, the curve passes through a maximum, after which it gradually diminishes to the final value of the conductance in pure ethyl alcohol. It is only in solutions in which the percentage of ethyl alcohol has fallen as low as 25 per cent that the curves begin to approach in form the fluidity curves of the mixtures. For mixtures containing larger amounts of acetone the form of the curve is due largely to the change in the ionization of the electrolyte. On the addition of a second solvent to acetone, the ionization of lithium bromide is greatly increased. In the water mixtures, the viscosity is increased so greatly for small additions of this solvent that the conductance diminishes. In the case of methyl alcohol, however, the fluidity is only slightly reduced by the addition of alcohol and consequently the conductance curve rises initially due to the increased ionization of the salt. At higher concentrations of alcohol, however, the increasing viscosity of the solvent finally makes itself felt and the conductance again falls. At the higher concentration of the salt, the addition of water causes a sufficient increase in the ionization of the electrolyte to overbalance the decrease due to the decreasing fluidity of the mixture. Initially, therefore, the conductance curve for lithium bromide in the mixture increases with the addition of water, passing through a slight maximum, after which the curve approximates the fluidity curve of the solvent.

As a rule, higher types of salts are ionized to a much smaller extent than are binary electrolytes, particularly the salts of metals which exhibit a pronounced tendency to form solvates with water. In Table LXXIX are given values for the conductance of calcium nitrate in mixtures of acetone with methyl and ethyl alcohols and water.[20]

The relation between the conductance and the composition of these mixtures is shown graphically in Figure 47. It is evident that solutions of calcium nitrate in mixtures containing acetone present a very complex

[20] Jones, Bingham and McMaster, *loc. cit.*, p. 193.

TABLE LXXIX.

CONDUCTANCE OF SOLUTIONS OF CALCIUM NITRATE IN MIXTURES OF ACETONE WITH METHYL AND ETHYL ALCOHOLS AND WATER AT 0°.

Per Cent Acetone	0	25	50	75	100	
H_2O	128.3	80.0	66.2	76.7	10.36	$V = 1600$
CH_3OH	77.2	82.6	79.2	64.2	10.36	
C_2H_5OH	18.81	31.6	38.0	36.2	10.36	
H_2O	89.8	55.0	42.2	31.3	4.44	$V = 10$
CH_3OH	18.98	17.76	13.82	8.10	4.44	
C_2H_5OH	5.13	6.01	6.00	4.80	4.44	

relation between conductance and composition. This is particularly true of the acetone-water mixtures. Solutions of calcium nitrate in acetone are ionized to a very slight extent, even at high dilutions. The limiting equivalent conductance of binary electrolytes in acetone has a value of approximately 170. The limiting value of the equivalent conductance of

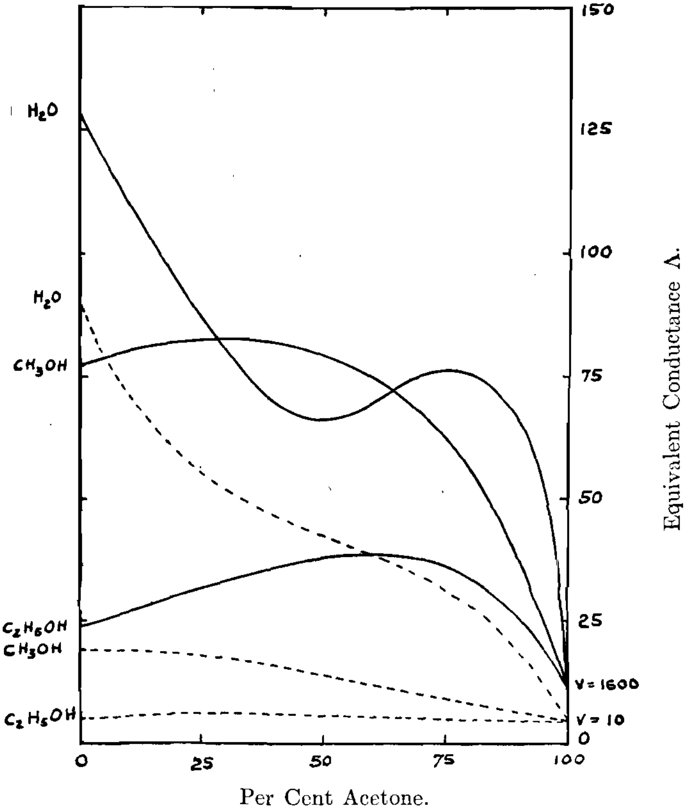

FIG. 47. Conductance of Calcium Nitrate in Acetone Mixtures at 0° at $V = 10$ and $V = 1600$.

calcium nitrate is obviously of the same order. Even at a dilution of 1600 liters, therefore, calcium nitrate is ionized less than 10 per cent. The addition of hydroxy-compounds, which tend to form stable complexes with calcium salts, causes an enormous increase in the conductance of solutions of this salt in acetone, even though the amount of the second component added is relatively small. The curves as drawn are only rough approximations and it is not improbable that the initial conductance increase is even greater than indicated in the figure. Owing to the increased ionization of calcium nitrate on the addition of water, therefore, the conductance rises enormously, even though the speed of the ions is greatly depressed on the addition of water. As a consequence, the conductance curve on addition of water passes through a pronounced maximum at a composition at or above 75 per cent of acetone. On the addition of further amounts of water, the conductance curve follows, roughly, the fluidity curve of the solvent mixture. The addition of methyl alcohol likewise results in an increase in ionization, although this increase is much lower than in the case of water. The conductance curve, therefore, passes through a comparatively flat maximum at a composition in the neighborhood of 25 per cent of acetone. The ionization of calcium nitrate dissolved in a mixture of methyl alcohol and acetone therefore has not reached a value corresponding to that of a normal electrolyte, even when as much as 75 per cent of methyl alcohol has been added. The addition of ethyl alcohol causes a marked increase in the conductance, although considerably less than that due to methyl alcohol. The curve passes through a distinct maximum, after which the conductance decreases, chiefly owing to the decrease in the fluidity of the mixture.

At the higher concentration, the curves are greatly modified. Again, the ionization of the electrolyte is greatly increased on addition of the second solvent, as is indicated by a marked increase in the conductance of the solutions. In the case of water, the curve exhibits a marked inflection point in the neighborhood of the composition containing 50 per cent of alcohol and water. At these higher concentrations, therefore, solutions of calcium nitrate in mixtures of acetone and water exhibit an ionization much below that of normal electrolytes. The curve, on addition of methyl alcohol, shows a continuous increase in the conductance throughout its course. That for ethyl alcohol shows a slight increase only, the curve exhibiting a very flat maximum. At the higher concentrations of the salt, therefore, the addition of ethyl alcohol causes only a relatively small increase in the conductance of calcium nitrate. Actually, however, the ionization is considerably increased on the addition of ethyl alcohol, since the fluidity of the ethyl alcohol mixture is much lower than that of pure acetone.

Extensive data are available which show that the examples given above are typical of the behavior of solutions of electrolytes in mixed solvents. The data do not have sufficient precision to make it possible to determine the values of Λ_0 in the mixtures, for which reason it is necessary to consider only the general outline of the conductance curves. It is evident that, in the case of solutions of salts which are highly ionized, the conductance curves parallel the fluidity curves. If, however, the electrolyte is only slightly ionized in one of the solvents, the addition of the second component may cause a large shift in the conductance values due, primarily, to a large change in the ionization of the electrolyte. It should be noted that, whenever the fluidity of the solvent medium changes, whether under the action of pressure or temperature, or whether through a change in the viscosity of the medium due to the presence of the electrolyte itself or due to the presence of a non-electrolyte, the conductance is affected by the viscosity change, and, while the conductance may not change in direct proportion to the fluidity change of the medium, nevertheless the effect of fluidity change is very marked. These facts are in entire accord with our notions as to the nature of the conduction process. On the other hand, it is clearly evident that the conductance is likewise dependent upon some other factor, namely the ionization. The ionization is a function, in the first place, of the dielectric constant of the solvent medium, as well as of the concentration of the electrolyte. In the second place, however, the ionization is greatly affected by interaction between the dissolved electrolyte and the solvent medium. Apparently, complexes are formed between the dissolved electrolyte and the solvent, which are largely ionized. Certain solvents, such as acetone, for example, appear to have a very small tendency to form complexes. When salts, which exhibit a marked tendency to form complexes, are dissolved in solvents of this type, the resulting ionization is relatively low. This effect is marked in the case of salts of the alkali metals. Salts of sodium, potassium, rubidium and caesium are very largely ionized in all solvents, apparently without exception, whereas the salts of lithium exhibit a markedly lower ionization in many solvents, as for example in acetone. As is well known, lithium salts exhibit a great affinity for hydroxy-solvents, and apparently the formation of a complex is a necessary condition for ionization in the case of salts of this type.

In comparing the ionizing power of different solvents, therefore, it is necessary to select such electrolytes as exhibit the least tendency to form complexes. This has in general been done by various writers on this subject. Nevertheless, it should be borne in mind that the possibility always exists that a given electrolyte in a given solvent may exhibit exceptional properties.

Chapter VIII.

Nature of the Carriers in Electrolytic Solutions.

1. *Interaction between the Ions and Polar Molecules.* The results given in the preceding chapter indicate that an equilibrium exists between the ions, and possibly the un-ionized fraction, of a dissolved electrolyte and the molecules of an added non-electrolyte of the polar type. If reactions of this type take place between a non-electrolyte and an electrolyte, both of which are present in relatively small amounts in the solvent medium, then there is all the more reason for believing that reaction takes place between the electrolyte and the non-electrolyte when the latter is present in large excess. Apparently, the ions in solution do not consist merely of the charged groups present in the original salt, but rather of these groups associated with the solvent. Where the ions possess great tendency to form definite complexes with the solvent, as is the case, for example, with the calcium ion in water and the silver ion in ammonia, a portion of the solvent is present in the form of a definite chemical compound. In addition to this, however, an ion may conceivably be associated with a further amount of solvent as a result of the charge on the ion and the electrical moment of the solvent molecules.

2. *Hydration of the Ions in Aqueous Solution.* It has been definitely established that in aqueous solutions certain ions are hydrated;[1] that is, in passing through the solution they carry water with them. Since the conductance values of all ions in water are of the same general order of magnitude, it follows that all ions are in all likelihood hydrated, save, perhaps, the highly complex ions.

If the ions are hydrated, then, in the course of a transference experiment, water will be transferred toward one electrode or the other. If N_w^a represents the number of molecules of water associated with the anion and N_w^c the number of molecules of water associated with the cation and if T_t^a is the fraction of the current carried by the anion, that

[1] Lobry de Bruyn, *Rec. Trav. Chim.* 22, 430 (1903); Morgan and Kanolt, *J. Am. Chem. Soc.* 28, 572 (1906); Buchböck, *Ztschr. f. phys. Chem.* 55, 563 (1906); Washburn, *J. Am. Chem. Soc.* 31, 322 (1909); Washburn and Millard, *J. Am. Chem. Soc.* 37, 694 (1915).

is, if this is the true transference number of the anion, and if T^c_t is the true transference number of the cation, then according to Washburn [2] the net transfer of water per equivalent of electricity passing through the solution will be:

$$T^c_t N^c_w - T^a_t N^a_w = N^F_w, \tag{47}$$

where N^F_w is the net transfer of water per equivalent of electricity.

In general, therefore, the passage of a current through a solution will be accompanied by a net transfer of water, whose value is N^F_w per equivalent of electricity. This transfer of water may be determined by introducing into the solution a substance which itself takes no part in the transfer of the charge. The change in the concentration of the water with respect to this reference substance will give the transfer of water, and the change in the concentration of the salt with respect to the same reference substance will give the true transference number of the salt at the same time. It follows, therefore, that if the true transference number of the salt and the net transference number of the water are known, the relative amounts of water associated with the two ions may be determined. As ordinarily carried out, transference experiments in which water is employed as reference substance yield, not the true transference number, but a transference number differing therefrom by an amount depending upon the relative amount of water transferred. The relation between the true and the ordinary transference number is given by the equation:

$$T^c_t = T^c_o + N^F_w\left(\frac{N_s}{N_w}\right), \tag{48}$$

where T^c_o is the ordinary transference number of the cation and $\frac{N_s}{N_w}$ is the ratio of the number of mols of salt to that of water in the solution. If transference measurements on various electrolytes with a common ion are carried out, then the relative hydration of the uncommon ions may be determined. The absolute hydration of the ions is of course not determinable. In Table LXXX are given values of the true transference number, the ordinary transference number, and the water transference

[2] Washburn, *loc. cit.*

number for different electrolytes in water at a concentration of 1.2 normal at 25°.

TABLE LXXX.

TRANSFERENCE NUMBERS OF ELECTROLYTES AND SOLVENT FOR AQUEOUS SOLUTIONS.

	HCl	CsCl	KCl	NaCl	LiCl
T_t^c	0.844	0.491	0.495	0.383	0.304
T_o^c	0.820	0.485	0.482	0.366	0.278
N_w^F	0.24	0.33	0.60	0.76	1.5

In solutions of these electrolytes, the net transfer of water takes place from the anode to the cathode, as shown by the values given in the table for N_w^F. In these cases, correspondingly, the true transference numbers of the cations are larger than the ordinary transference numbers. It is obvious from Equation 48 that, as the concentration of the solution decreases, the ordinary transference number approaches the true transference number. The relation between the water carried by the cation and that by the chloride ion is evidently given by the following equations:

$$
\begin{aligned}
N_w^{\mathrm{H}} &= 0.28 + 1.085\ N_w^{\mathrm{Cl}}, \\
N_w^{\mathrm{Cs}} &= 0.67 + 1.03\ N_w^{\mathrm{Cl}}, \\
N_w^{\mathrm{K}} &= 1.3 + 1.02\ N_w^{\mathrm{Cl}}, \\
N_w^{\mathrm{Na}} &= 2.0 + 1.61\ N_w^{\mathrm{Cl}}, \\
N_w^{\mathrm{Li}} &= 4.7 + 2.29\ N_w^{\mathrm{Cl}},
\end{aligned} \tag{49}
$$

Since the hydration of the chloride ion is not known, the absolute hydration of the various cations may not be determined. If, however, a value is assumed for the hydration of the chloride ion, then the hydration of the other ions may at once be calculated by means of these equations. The values of the hydration of the different cations for different assumed values for the hydration of the chloride ion are given in the following table:

TABLE LXXXI.

Calculated Hydration of the Ions for Different Assumed Values for the Hydration of the Chloride Ion.

N_w^{Cl}	N_w^{H}	N_w^{Cs}	N_w^{K}	N_w^{Na}	N_w^{Li}
0	0.28	0.67	1.3	2.0	4.7
4	1.0	4.7	5.4	8.4	14.
9	2.0	9.9	10.5	16.6	25.3

The assumption that the chloride ion is un-hydrated is improbable, since the conductance of the chloride ion is very nearly equal to that of the potassium ion. The value assumed for the hydration of the chloride ion should therefore differ little from that of the potassium ion. This necessitates assuming for the chloride ion a value not materially less than 4. *In all likelihood the true value lies somewhere between 3 and 9,* although the true value must necessarily remain uncertain. Below are given the values of the ionic conductance for the different ions at 18°, together with the ratio of these conductances to that of the hydrogen ion.

TABLE LXXXII.

Comparison of Ionic Conductances and Hydration Numbers.

	N_w^{Cl}	N_w^{H}	N_w^{Cs}	N_w^{K}	N_w^{Na}	N_w^{Li}
Hydration No.	4.0	1.0	4.7	5.4	8.4	14.0
Ionic Cond.	65.5	315.	68.0	64.5	43.4	33.3
$315/\Lambda$	4.8	1.0	4.6	4.9	7.3	9.5

It is seen that the values of the ionic conductances relative to that of the hydrogen ion correspond roughly with the values of the hydration of the different ions, assuming the hydration of the hydrogen ions to be unity. An exact correspondence between the hydration and the conductance is not to be expected. Nevertheless, except in the case of the caesium and the chloride ions, the order of the reciprocal conductance values corresponds with the order of the hydration numbers. The chloride, caesium, and potassium ions are among the most rapidly moving ions in water, excepting the hydrogen and hydroxyl ions, and it may therefore be concluded that all ions in water are hydrated at least as much as the chloride ion. It is possible, of course, that the hydration numbers may be considerably larger than those assumed on the basis of an hydration of 4 for the chloride ion. How the hydration of the ions

varies with the temperature and the concentration is not known. If the absolute hydration of the ions is large, then it is to be expected that the hydration will change at higher concentrations. It is possible, therefore, that at concentrations below 1.2 normal the hydration of the ions may be considerably greater than at the higher concentration.

As we have seen in an earlier section, at higher temperatures the conductance of the more rapidly moving ions approaches that of the more slowly moving ions. At the same time, as we have seen, the conductance of the more slowly moving ions changes almost in exact proportion to the fluidity change of the solvent. It may be concluded, therefore, that, at higher temperatures, the hydration of the more rapidly moving ions increases and approaches that of the more slowly moving ions, such as that of the lithium ion. It is probable, therefore, that as the temperature increases the net transference of water diminishes, while the absolute amount of water associated with the ions increases.

3. *Calculation of Ion Dimensions from Conductance Data.* Lorenz[2a] has calculated the ion dimensions from the ion conductances, by means of the Einstein-Stokes[2b] equation. The values obtained for the ion dimensions have been compared with those obtained by other methods, as determined from the density of substances in a condensed state, assuming close packing of the molecules. For ions containing a large number of atoms, particularly large organic anions and cations, the calculated values from the conductance data agree well with those derived by other methods. In the case of the simpler ions, however, a similar agreement has not been found. In the case of the alkali metals, for example, lithium, which has the smallest atomic volume, has the lowest conductance, while caesium, with the largest atomic volume, has the highest conductance. It has generally been assumed that the reversal in the order of the conductance of the ions of the alkali metals is due to hydration.

Born[2c] and Lorenz[2d] consider that the Einstein-Stokes equation is applicable even in the case of small ions and that the observed divergence is due to electrical interaction between the charge on the ions and the adjacent solvent molecules. This electromagnetic frictional effect is the greater, the smaller the volume of the ion. The total frictional effect which the ion experiences is thus the sum of two effects, one of which decreases and the other of which increases with decreasing ionic diameter. The function which expresses the ionic resistance in terms

[2a] Lorenz, *Ztschr. f. Elektroch.* 26, 424 (1920); *Ztschr. f. phys. Chem.* 73, 252 (1910); also, numerous articles in the *Ztschr. f. Anorg. Chem.*

[2b] Einstein, *Ann. d. Phys.* 17, 549 (1905).

[2c] Born, *Ztschr. f. Elektroch.* 26, 401 (1920).

[2d] Lorenz, *loc. cit.*

of the ionic diameter therefore passes through a minimum. In this way Born accounts for the diminishing values of the ion conductance with decreasing volume in the case of the simpler ions.

The constants involved in the equation for the electro-frictional effect are somewhat uncertain. In any case, these constants should depend solely upon the properties of the solvent medium, assuming an ion of fixed dimensions.

The correctness of this theory appears somewhat doubtful. In the first place, it is difficult to account for the fact that at higher temperatures the ion conductances in aqueous solutions approach the same value. While it is true that the dielectric constant of the medium varies with the temperature, an effect of the order of that observed in aqueous solutions is scarcely to be expected. More convincing, perhaps, is the relation of the ion conductances in non-aqueous solutions. If the theory of Born and Lorenz is correct, the order of the ion conductances should be the same in different solvents. This is by no means the case. For example, as may be seen from the values of the ion conductances in liquid ammonia given in an earlier chapter, the conductance of the silver ion is markedly lower than that of the sodium ion in ammonia; while in water the conductance of the sodium ion is much smaller than that of the silver ion. Again, the conductance of the ammonium ion in ammonia is practically identical with that of the sodium ion, whereas the conductance of the ammonium ion in water is almost identical with that of the potassium ion. While the conductance of the lithium ion in water is much smaller than that of the silver ion, the conductance of the lithium ion in ammonia differs but little from that of the silver ion. So, also, in the case of anions, the conductance of the nitrate ion is identical with that of the iodide ion in ammonia, while in water it is much smaller. Similarly, the conductance of the chloride ion in ammonia is markedly greater than that of the iodide ion; whereas in water the conductance of the iodide ion is greater than that of the chloride ion. An examination of the conductance values of electrolytes in other non-aqueous solvents shows that here, too, the order of ion conductances is a characteristic property of the solvent medium and of the dissolved electrolytes. For example, in acetone the conductance values of the lithium, sodium and potassium ions are practically identical; while the conductance of the ammonium ion is markedly greater than that of the potassium ion. While in water the conductance of the sulphocyanate ion is markedly lower than that of the iodide ion, in acetone the conductance of this ion is greater than that of the iodide ion. So, also, in pyridine the con-

ductance of the sulphocyanate ion is markedly greater than that of the iodide ion.

It is evident that, applied to solutions in non-aqueous solvents, the theory of Born and Lorenz meets with great difficulties. The values of the ion conductances in different solvents are in much better agreement with the assumption that the differences in the ion velocities of the simpler ions are primarily due to the size and nature of the complexes formed between the ion and the solvent medium. An ion will, in general, exhibit a low conductance in a medium with which it has a great tendency to form stable complexes. On the other hand, in media with which the tendency to form complexes is less pronounced, its conductance will be relatively high. Thus, the silver and ammonium ions in ammonia have a relatively low conductance; while in acetone, sodium and lithium have a relatively high conductance. The properties of solutions of these salts in the solvents mentioned indicate a high solvation in ammonia solutions and a low solvation in acetone solutions.

It has been demonstrated by means of transference measurements in aqueous solutions that the alkali metal and hydrogen ions are hydrated. While the absolute degree of hydration remains uncertain, it is probably safe to assume that the hydration of the hydrogen ion is not less than unity, which requires a hydration in the neighborhood of 5 for the potassium ion and 14 for the lithium ion.

As we have seen in Chapter V, the relation between the conductance, *i.e.*, the speed of an ion, and the viscosity of the medium through which it moves is anything but simple. The conductance of ions of small dimensions is not proportional to the fluidity of the ionizing solvent. On the addition of a second non-ionic component, the conductance change of the ion is approximately proportional to the fluidity change of the medium only when the molecules of the added substance are small. When the dimensions of the molecules of the added substance are large compared with those of the ions, the conductance change is invariably smaller than the fluidity change.

Finally, Dummer [2e] has measured the diffusion coefficients of a number of organic solvents of varying molecular volume in one another and compared his results with one another by means of the Einstein-Stokes equation. The molecular dimensions found for the same substance in different solvents do not agree well with one another. The Einstein-Stokes equation should be applied with caution to systems of particles of molecular dimensions.

[2e] Dummer, *Ztschr. f. anorg. Chem.* *109*, 31 (1919). Compare also, Öholm, *Medd. K. Vetens-Akad's Nobelinstitut*, Nos. 23, 24 and 26 (1912).

4. *The Hydrogen and Hydroxyl Ions.* In aqueous solutions, the hydrogen and hydroxyl ions appear to occupy a more or less unique position. They are characterized by the exceptionally high value of their ionic conductance. At 0°, the hydrogen ion moves approximately 10 times as fast as the acetate ion, or approximately 5 times as fast as the potassium ion. At the same temperature the hydroxyl ion moves from 5 to 6 times as fast as the acetate ion. The question as to the cause of the high values for the conductance of these two ions in water naturally arises. A more or less obvious explanation is: that these ions are hydrated to a much smaller extent than are the other ions; or, in other words, they are relatively smaller than the other ions. This view, moreover, is supported by the results obtained from transference experiments. As was shown in the preceding section, the amount of water associated with the hydrogen ion is much smaller than that associated with any other positive ion for which data exist. It might be expected, therefore, that the speed of the hydrogen ion would have an abnormally high value because of its low hydration. Presumably, a similar explanation would hold in the case of the hydroxyl ion, although here we have no data as to the relative hydration. That the hydrogen ion is in fact hydrated, admits of no question. The minimum amount of water which might be associated with the hydrogen ion is 0.28 mol. It is improbable, however, that hydrogen ions exist in water unassociated with water molecules. In an earlier section it was shown that the addition of water to alcohol solutions of the strong acids greatly diminishes the conductance of the acid, while the addition of water to a solution of a weak acid greatly increases the conductance of the acid. It may be inferred from this that a complex is formed between the hydrogen ion and the added water whose speed is much lower than that of the normal hydrogen ion in alcohol. In the case of the weak acids, the addition of water increases the ionization, owing to the formation of a complex between water and the acid.

The formation of a more or less definite complex between an acid and water is moreover indicated by the large energy change accompanying the solution of acids in water. It has been suggested that the hydrogen ion is indeed an oxonium ion, bearing the same relation to oxygen that the ammonium ion does to nitrogen. The hydrogen ion would therefore be OH_3^+. That the oxygen compounds form salt-like substances with the halogen acids is further borne out by the fact that oxygen compounds dissolved in the liquid halogen acids almost invariably yield electrolytic solutions, some of which are ionized almost as much as the typical salts.[3] At the same time it has been shown that the organic

[3] Archibald, *Journal de Chimie Physique*, *11*, 741 (1913).

substance is associated with the cation.[4] In the case of sulphur, which element is closely related to oxygen, salts of the type R_3SX are well known.

Correspondingly, the ammonium salts dissolved in liquid ammonia exhibit all the properties of acids, and the ammonium ion exhibits the properties characteristic of the hydrogen ion.[5] If this conception regarding the nature of the hydrogen ion is correct, we should expect solutions of the acids in solvents, which do not possess the power of forming complexes of the type R_3O^+, to be relatively poor conductors. Such indeed appears to be the case. Dissolved in the alcohols, hydrogen chloride conducts fairly well; while dissolved in acetone,[6] hydrogen chloride yields a solution of very low conducting power. In view of the fairly high dielectric constant of acetone, it is difficult to account for this behavior of the acid except on the assumption that in this case there is little tendency to form the oxonium complex. There are no data to indicate that hydrogen chloride is a conductor when dissolved in sulphur dioxide or any other solvent which does not contain oxygen, nitrogen or other atoms capable of forming complexes.

These various facts indicate that the hydrogen ion in water is, in fact, not a hydrogen ion, but an oxonium ion. Whether the charge is associated with the hydrogen or with the oxygen atom cannot be determined in this case any more than it can in that of the similar ammonium salts. It appears likely, however, that in salts of this type the charge is associated either with the oxygen or nitrogen atom, or with the group as a whole, rather than with one of the hydrogen atoms.

5. *Ions of Abnormally High Conductance.* Certain writers have sought to relate the abnormally high conductance of the hydrogen and hydroxyl ions with the fact that these ions are products of the ionization of the solvent itself.[7] They have therefore adopted a theory founded upon the old theory of Grotthuss,[8] according to which the mechanism of the conduction process consists, not in a transfer of the ions through the solution, but in an ordered arrangement of the polar molecules of the electrolyte, alternately positive and negative, in accordance with the impressed field. An interchange of positive and negative carriers takes place between adjacent molecules resulting thus in a separation of the products at the two electrodes. The work of Faraday and Hittorf has definitely overthrown the theory of Grotthuss, but these later writers

[4] Steele, McIntosh and Archibald, *Ztschr. f. phys. Chem.* 55, 176 (1906).
[5] Franklin and Kraus, *Am. Chem. J.* 23, 304 (1900); Franklin and Stafford, *Am. Chem. J.* 28, 83 (1902); Franklin, *Am. Chem. J.* 47, 285 (1912).
[6] Lucasse, Thesis, Clark Univ., 1920.
[7] Danneel, *Ztschr. f. Electroch.* 11, 249 (1905); Hantzsch and Caldwell, *Ztschr. f. phys. Chem.* 58, 575 (1907).
[8] *Ann. d. Chim.* 58, 54 (1806).

assume that, in the case of the hydrogen and the hydroxyl ions in water, an interchange takes place between the ions and the solvent molecules with the result that the mean path over which these ions travel is reduced in proportion to the effective diameter of the solvent molecules which are concerned in the interchange. *A priori*, there is nothing to indicate that this hypothesis may not be correct. If it is correct, however, it must lead to certain definite consequences which we may now examine.

In the first place, it is to be expected that a similar phenomenon will be found in solutions in non-aqueous solvents which are capable of furnishing ions. In the case of liquid ammonia an equilibrium exists of the type:

$$NH_3 = NH_2^- + H^+;$$

or, perhaps,

$$2NH_3 = NH_2^- + NH_4^+,$$

where NH_4^+ is the ammonium ion and NH_2^- is the basic ion of liquid ammonia. That such an equilibrium exists, is indicated by the fact that certain ammonolytic equilibria exist in ammonia solutions comparable in all respects with hydrolytic equilibria in aqueous solutions.[9] On the basis of the above hypothesis, we should expect that the ammonium ions and the NH_2^- ions would exhibit an exceptionally high conducting power in liquid ammonia solutions. As may be seen by referring to the table of ionic conductances in Chapter II, the amide ion in liquid ammonia possesses a conducting power markedly lower than that of typical negative ions, while the conductance of the ammonium ion is distinctly lower than that of the potassium ion. It follows, therefore, that in ammonia solutions the ammonium and the amide ions are in no wise exceptional. It has been maintained that the conductance of the alcoholate ion in the alcohols is abnormally high. According to the best data available, however, the conductance of the alcoholates in alcohol [10] is of the same order as that of typical salts in these solvents.

As a result of conductance and transference measurements with the formates in formic acid it has been shown that the formate ion in formic acid possesses an exceptionally high conducting power. While the precise values are somewhat uncertain, roughly, the ionic conductances of the sodium, potassium and formate ions in formic acid at 25° are 14.6, 17.5 and 51.6.[11] The limiting value of the conductance of hydrochloric acid in formic acid is approximately 75, compared with the value 69.4 [12]

[9] Franklin, *J. Am. Chem. Soc.* 27, 820 (1905).
[10] Robertson and Acree, *Intern. Congr. Appd. Chem.* [8] 26, 609 (1912).
[11] Schlesinger and Bunting, *J. Am. Chem. Soc.* 41, 1934 (1919).
[12] Schlesinger and Martin, *J. Am. Chem. Soc.* 36, 1618 (1914).

for potassium formate, for example. Since the transference number of hydrochloric acid in formic acid is not known, it is uncertain whether or not the hydrogen ion in formic acid possesses an abnormally high conducting power. The evidence, however, indicates that the chloride ion possesses a conducting power not greatly smaller than that of the formate or hydrogen ion. The limiting value of the conductance of ammonium chloride can scarcely be lower than 52.[13] The value is somewhat uncertain because of the solvolytic reaction between the salt and the solvent. However, assuming probable values for the ionization constants of ammonium formate and hydrochloric acid and pure formic acid, it can be shown that the fraction of salt transformed to acid and base by reaction with the solvent cannot affect the conductance by more than a few units. If we assume, therefore, the value 52 for the limiting value of the equivalent conductance of ammonium chloride, and assuming for the conductance of the ammonium ion the value 18.8, which follows from the value 70.4 for the limiting value of the equivalent conductance of ammonium formate, we obtain for the limiting value of the conductance of the chloride ion the value 33.2 and for the hydrogen ion 42.8. This indicates that the conductance of the hydrogen ion in formic acid does not differ greatly from that of the chloride ion in the same solvent. The exceptionally high value found for the conductance of the hydrogen and the formate ions, like that of the chloride ion, is presumably due to the relatively smaller dimensions of these ions compared with those of the positive ions in formic acid.

It has also been suggested that the pyridonium ion, $C_6H_5NH^+$, possesses an abnormally high conducting power in pyridine.[14] This, however, rests upon a false accepted value for the conductance of typical salts in pyridine. The conductance of pyridine hydrochloride at a dilution of 32 liters and 25° in pyridine has been found to be 27.4. The conductance of sodium iodide in pyridine at a dilution of 57.7 liters and 18° is 23.6.[15] In general, at these concentrations, the conductance of solutions in pyridine changes but little with concentration. Consequently the conductance of sodium iodide in pyridine at 32 liters would differ but little from that at the lower concentration. On the other hand, the conductance at 18° is materially lower than at 25° because of the greater viscosity of the solution at the lower temperature. Assuming a viscosity correction of two per cent per degree the conductance of sodium iodide at 25° would be approximately 27.0. In other words, the con-

[13] Schlesinger and Calvert, *J. Am. Chem. Soc.* 33, 1924 (1911).
[14] Hantzsch and Caldwell, *loc. cit.*
[15] Ottiker, Dissertation, Lausanne (1907); Kraus and Bray, *J. Am. Chem. Soc.* 35, 1379 (1913).

ductance of a typical salt in pyridine differs but little from that of a salt of the solvent itself.

While, therefore, there are cases in which the ions common to the solvent exhibit an abnormally high conducting power, as they do in water at ordinary temperatures, there are other cases in which the conducting power of these ions is entirely normal. In this connection it is to be borne in mind that with rising temperature the speed of the hydrogen and hydroxyl ions in water approaches that of the more slowly moving ions. At 306° the conductance of the hydrogen ion differs from that of the potassium ion less than the conductance of the potassium ion differs from that of the acetate ion at ordinary temperatures. As has been pointed out, the relative decrease in the speed of the more rapidly moving ions at higher temperatures is due to the increase in the size of the more rapidly moving ions. It seems more rational, therefore, to ascribe the abnormally high speed of the hydrogen and hydroxyl ions in water to the low value of their hydration, which moreover is in accord with the experimentally determined values of the relative hydration of the different ions in water at ordinary temperatures.

While it cannot be definitely stated that all hydrogen ions in water are associated with at least one molecule of water, it nevertheless appears probable that such is the case. Were the hydrogen ion unhydrated, we should expect a much greater value for the conductance of the hydrogen ion. In the case of liquid ammonia solutions, it has been shown that the speed of the negative electron, which at low concentrations is associated with at least one ammonia molecule, is approximately seven times that of the sodium ion. It seems not unlikely that the negative electron in dilute solutions is actually associated with a greater number of ammonia molecules. Taking all these facts into consideration, it appears probable that the hydrogen ion is associated with at least one molecule of water.

It is evident that our conception as to the nature of the ions has undergone a great amplification during the past twenty years. Prior to that time the ion of an element was looked upon merely as an atom of the element associated with a charge. Now, however, we know that the ions consist of more or less definite complexes containing the solvent, and the nature and dimensions of these complexes depend, not alone upon the properties of the electrolyte and of the solvent, but also upon the condition under which the solution exists, such as concentration, temperature, pressure, etc.

6. *The Complex Metal-Ammonia Salts.* A number of salts of the heavy metals, particularly those of cobalt, chromium and the platinum metals, form series of compounds with ammonia in which there appears

a remarkable relationship between the number of ammonia molecules associated with the complex salt and the properties of the salt, both in solution and in a crystalline state. While the compounds containing ammonia, or ammonia derivatives, are, in general, the most stable representatives of this class, many other compounds are known where other molecules function in a manner similar to those of ammonia. These complex salts have been studied extensively by a number of investigators, notably by Werner,[16] who has proposed a theory of the constitution of these compounds which has met with remarkable success in accounting for their properties. It is not proposed to give here an extended exposition of Werner's theory, since that is beyond the scope of this monograph. However, a brief outline may be given here, in order to make intelligible the relation between the constitution of the complex metal-ammonia salts and their ionic properties.

According to Werner's theory, the strongly electronegative elements or groups of elements are attached to the nuclear atom by what are termed principal valences, while neutral groups of molecules such as ammonia are associated with the nuclear atom by auxiliary or secondary valences. A definite number of atoms or groups is always attached to the nuclear atom, either by principal or secondary valences, and this number, which is usually 6 and sometimes 4, is fixed. The number of atoms or groups so attached is called the co-ordination number. The charge on the nuclear complex depends upon the number of principal valences comprised within the co-ordination number. If N is the normal valence of the nuclear atom, C the co-ordination number of the nuclear group, and n the number of secondary valences satisfied in the nuclear group by neutral complexes, such as ammonia, etc., then the number of charges on the nuclear group or complex is: $q = N - C + n$. Usually the co-ordination number is 6 or 4. If, for example, the co-ordination number is 6 and the normal valence of the nuclear atom is 4, then, if $n = 2$, that is if two molecules are associated in the nuclear complex, $q = 0$, and the charge on the complex will be zero. If, on the other hand, n were 0, the charge on the nuclear complex would be -2; that is, the nuclear complex would carry two negative charges. On the other hand, if n were 6, $q = +4$; that is, the nuclear complex would carry 4 positive charges. For a co-ordination number 6, the maximum variation in the charge on the nuclear complex is from 4 positive to 2 negative charges. An example will serve to make the relationships clear. Platinum chloride, $PtCl_4$, in which platinum appears with the principal valence of 4, forms with ammonia the following series of complexes, all of which are known except the second.

[16] Werner, New Ideas on Inorganic Chemistry. *Trans. by E. P. Hedley, 1911.*

1	2	3	4	5	6	7
$[Pt(NH_3)_6]Cl_4$	$[Pt^{(NH_3)_5}_{Cl}]Cl_3$	$[Pt^{(NH_3)_4}_{Cl_2}]Cl_2$	$[Pt^{(NH_3)_3}_{Cl_3}]Cl$	$[Pt^{(NH_3)_2}_{Cl_4}]$	$[Pt^{NH_3}_{Cl_5}]K$	$[PtCl_6]K_2$
Chloride of Drechsel's base	Unknown	Platini-diammine chloride	Platinimono-diammine chloride	Platini-diammine chloride	Cossa's second salt	Potassium platinum chloride

Those elements or groups appearing with platinum within the brackets are contained in the nucleus, while those without the brackets carry charges and are capable of ionization. The co-ordination number of platinum in the nucleus is 6. The charge on the nucleus is therefore given by the equation $q = 4 - 6 + n$, where n is the number of ammonia molecules in the complex. In the first compound $[Pt(NH_3)_6]Cl_4$, $n = 6$ and $q = +4$. This compound therefore ionizes according to the equation: $[Pt(NH_3)_6]Cl_4 = [Pt(NH_3)_6]^{++++} + 4Cl^-$. On the other hand, in the compound $[PtCl_6]K_2$, $n = 0$ and $q = -2$. This compound, therefore, ionizes according to the equation: $[PtCl_6]K_2 = PtCl_6^{--} + 2K^+$. The manner in which the ionization takes place in the other compounds may obviously be derived from the equation given. If Werner's theory is correct, then, when the various compounds are dissolved in water, the conductance of the resulting solutions should vary in correspondence with the number of changes involved in the ionization reaction. At low concentrations, the conductance of the first compound should lie in the neighborhood of 500; that of the third compound, in the neighborhood of 200; that of the fourth, in the neighborhood of 100; while that of the fifth should be zero. On the other hand, that of the sixth should lie in the neighborhood of 100 and that of the seventh in the neighborhood of 200. In solutions of these last two compounds, the platinum complex should appear as anion. This consequence of Werner's theory has been confirmed by experiment. The conductance of the first, third, fourth, fifth, sixth and seventh compounds at 0° and at a dilution of 1000 liters are respectively: 522.9, 228, 96.75, 0, 108.5, and 256.

The conductance of the fifth compound is actually not quite zero, since in solution compounds of this type are not entirely stable and reaction takes place with the water, wherein molecules of water enter the nucleus and thus produce a charged complex, the water functioning in a manner similar to that of ammonia. However, in many cases values of Λ less than unity have been obtained, and it has been shown that the conductance is a function of the time and that, moreover, the reaction is catalyzed at the electrode surfaces.[16a]

There can be no doubt but that the ionization of the complex metal-ammonia and other similar salts depends upon the combination of am-

[16a] Werner and Herty, *Ztschr. f. phys. Chem.* 38, 331 (1901).

monia with the nuclear atom. What characterizes these compounds in particular is their stability. Similar relations may exist in the case of other salts which show a pronounced tendency to form complexes, such as calcium salts for example, but in these cases reaction between the complex and the solvent medium takes place very rapidly. The behavior of these complexes in water does not differ greatly from that of calcium chloride in propyl alcohol, whose ionization is greatly increased on the addition of water. On the other hand, it is to be borne in mind that in non-aqueous solutions those salts which exhibit only a slight tendency to form complexes with water are highly ionized in all cases. This is particularly true, for example, of potassium salts. It appears probable that such salts do not form complexes similar to the metal-ammonia salts. It is probable, however, as we have seen, that all ions are hydrated. It appears likely that the solvent molecules may be associated with the ions in several ways. Certain of the solvent molecules may be combined in a more or less definite manner, as in the metal-ammonia complexes, while other molecules may be associated with the ions due to the operation of purely electrical forces.

7. *Positive Ions of Organic Bases.* With the exception of ions of salts of organic bases and a few salts of the type of the ammonium salts, the positive ions consist essentially of metallic elements. This tendency of the metallic elements to form electropositive ions is in harmony with prevailing conceptions regarding atomic structure. The organic bases are derived from the less electropositive elements on the introduction of organic radicals, such as alkyl and aryl radicals, into combination with the nuclear element. The number of carbon radicals introduced depends upon the valence of the element in question, and upon its position in the periodic system. For elements up to the fifth group, the organic bases have the constitution: $R_{n-1}M^nX$, where n is the maximum valence of the element with respect to negative elements. For elements of the fifth to the seventh groups, inclusive, the bases have the constitution: $R_{n+1}M^nX$, where n is the valence of the element toward hydrogen. Thus, we have the organic bases: CH_3HgOH, $(CH_3)_2TlOH$, $(CH_3)_3SnOH$, $(CH_3)_4NOH$, $(CH_3)_3SOH$ and $(C_6H_5)_2IOH$. The strength of the organic bases depends upon their constitution. As hydrogen is substituted by organic groups, particularly alkyl groups, the strength of the base in general increases, although a marked increase does not take place until the substitution of the last hydrogen atom occurs, in which case the resulting base exhibits a maximum strength. Thus, monomethyl-, dimethyl- and trimethylammonium hydroxides are comparatively weak bases, while

tetramethylammonium hydroxide is a base whose strength is practically the same as that of potassium hydroxide. The positive ions of the strong organic bases possess distinct metallic characteristics in their compounds. With a few exceptions, these ionic groups may not be obtained in a free neutral state, since in this condition they are comparatively unstable, yielding, as a rule, various neutral organic compounds. The tetramethylammonium group, as indeed the ammonium group itself, possesses an appreciable stability. So, for example, the ammonium group forms an amalgam in which the presence of the free ammonium group has been established.[17] The tetramethylammonium group forms a stable, solid, metallic amalgam with mercury,[18] and this group, moreover, may be precipitated in a free state by electrolysis in ammonia solution.[19] Under these conditions the free group dissolves in ammonia to form a solution which resembles solutions of the alkali metals in the same solvent. These solutions, however, are relatively unstable so that their properties have not been further investigated.

The mercury group, CH_3Hg, has been obtained in a free state by electrolytic precipitation from an ammonia solution.[20] The free group is a distinctly metallic substance which is a good conductor of the electric current. This group, while relatively stable in comparison with other groups, nevertheless reacts slowly, even at low temperatures, and at high temperatures it reacts instantaneously according to the equation:

$$2CH_3Hg = Hg + Hg(CH_3)_2.$$

Not only do the ions of the organic bases, therefore, resemble the metallic elements, but the free basic groups themselves, when they possess sufficient stability to admit of their being isolated, exhibit metallic properties. The metallic state of a substance is not one characteristic merely of elements which themselves are metallic in the elementary condition, but includes likewise various groups of elements whose constitution is such that they carry a negative electron which is relatively loosely attached to the group.

8. *Complex Anions.* Our knowledge of the structure of anion complexes is comparatively limited. No data are so far available which definitely establish that the anions in water are hydrated. It is true, that, from the conductance values of the anions and the hydration values of the cations, it may be inferred that the anions are likewise hydrated, but the hydration of the anions has not been experimentally verified.

[17] Coehn, *Ztschr. f. Anorg. Chem.* 25, 430 (1900).
[18] McCoy and Moore, *J. Am. Chem. Soc.* 33, 273 (1911).
[19] Palmaer, *Ztschr. g. Electroch.* 8, 729 (1902); Kraus, *J. Am. Chem. Soc.* 35, 1732 (1913).
[20] *Kraus, loc. cit.*

The existence of definite anion-complexes comparable, for example, with those of the cobalt and chromium salts is not indicated by the properties of electrolytes, either in solution or in the solid and liquid state. The anions often consist of definite groups containing one or more electronegative atoms. Among these we have, for example, the nitrates, chlorates, sulphates and other common anions, as well as many anions of organic acids. So far as the degree of ionization is concerned, salts of compound anions exhibit properties similar to those of salts of simple anions. The ionization of the hydrogen derivatives, namely the acids, of such anions, however, is largely dependent upon the nature of the atoms occurring in the anion complex. The introduction of strongly electronegative elements into the anion complex increases the strength, that is, the ionization of the acid. This behavior of the acids is so well known that details need not be introduced here.

Certain elementary ions form complex anions with the same or other elements, a more or less complex equilibrium existing among the various complex anions formed in solution. The most common example of a complex anion of this type is the complex iodide ion which is formed by the direct interaction of the iodide ion with iodine, forming the ion $I^-.I_2$. The equilibrium in the case of the tri-iodide ion has been extensively studied by a number of investigators. The mean composition of the solution in such cases depends upon the concentration, since the equilibrium between the simple and the complex ion is a function of the concentration.[21]

It is well known that the halogen salts form various complexes with other halogens, thus indicating that complex anions are formed between a halogen ion of one element with other elements of the halogen group. The chlor-iodides are familiar examples of this type. The equilibrium in the case of these complex anions has not been extensively studied.

The work of Küster [22] indicates that the normal sulphide ion reacts with excess sulphur to form a series of complex sulphur anions. These anions appear to be comparable with the complex iodide ion, the charge being associated with the original sulphide anion. The mean composition of a solution of sodium sulphide in equilibrium with free sulphur varies as a function of the concentration. The problem in the case of aqueous solutions is complicated owing to hydrolysis. The behavior of aqueous solutions of the alkali selenides and tellurides indicates that these metals also form complex anions in the presence of excess of these metals.[23] They have not, however, been extensively investigated.

[21] Bray and MacKay, *J. Am. Chem. Soc.* *32*, 915 (1910).
[22] Küster and Heberlein, *Ztschr. f. Anorg. Chem.* *43*, 53 (1905); Küster, *ibid.*, *44*, 431 (1905).
[23] Tibbals, *J. Am. Chem. Soc.* *31*, 902 (1909).

Solutions of complex selenides and tellurides have been obtained in liquid ammonia by the action of the normal salts on the free elements.[24] Solutions of the complex tellurides in liquid ammonia are the only ones which so far have been extensively investigated. The normal telluride, which is only slightly soluble in ammonia, is formed by the direct action of the metal on sodium in ammonia solution. The telluride so formed is a white substance, apparently somewhat crystalline in character. In the presence of excess tellurium the normal telluride reacts with the metal, forming a complex tellurium salt which is very soluble in ammonia. The composition of the solution in equilibrium with a normal telluride Na_2Te is Na_2Te_2.[25] Apparently the following reaction takes place:

$$Na_2Te_{\text{solid}} + Te_{\text{solid}} = Na_2Te_{2\ \text{solution}}.$$

This solution exhibits an intense violet blue color. When the normal telluride Na_2Te has disappeared, the complex Na_2Te_2 in solution reacts with free tellurium to form another complex. In concentrated solutions the composition of the ammonia solution corresponds very nearly with Na_2Te_4. The exact value of the composition, however, is a function of the concentration, the amount of tellurium in solution decreasing at lower concentrations.[26] The color of the solution in equilibrium with metallic tellurium is deep red.

The molecular weight of the telluride in equilibrium with metallic tellurium has been determined and found to correspond with the formula $Na_2Te.Te_x$; that is, sodium is associated with a divalent complex tellurium anion.[27]

While the normal telluride is a white substance exhibiting only non-metallic characteristics, the product resulting on evaporating a solution containing larger amounts of tellurium is metallic in appearance, indicating that the salts of the complex tellurides are metallic substances. This behavior of the complex tellurides in the free state is particularly important when we come to consider similar complex anions of metals of the fourth and fifth groups.

Whereas our knowledge of the complex anions of this type has previously been restricted chiefly to elements of the sixth and seventh groups, in recent years, through a study of solutions in liquid ammonia, evidence has come to light which indicates that the elements of the fourth and fifth groups form complex anions similar in character to the complex sulphide and iodide ions. In the case of the salts of these com-

[24] Hugot, *Compt. rend.*, *129*, 299 and 388 (1899).
[25] Chiu, Dissertation, Clark University (1920).
[26] E.g. Chiu, *loc. cit.*
[27] E. H. Zeitfuchs, Dissertation, Clark University (1921).

plex anions, however, the non-metallic characteristics have disappeared, and these substances in the solid state are metals. In solution, however, they exhibit properties similar to those of tellurium. A characteristic property of such solutions is the existence of anions of distinctly metallic elements. Thus, lead is precipitated on the anode when the current is passed through a solution containing the complex $Na_4Pb.Pb_x$.[28] A similar result has been obtained in the case of the antimony complex $Na_3Sb.Sb_x$.[29] In a solution of the lead complex in equilibrium with lead, 2.25 atoms of lead are precipitated on the anode per equivalent of electricity.[30] This corresponds with the mean composition of the solution. The proportion of lead to sodium in the presence of excess lead is independent of the concentration of the solution. In the case of the antimony complex, the mean composition of the solution is a function of the concentration. The maximum lies in the neighborhood of 0.4 N sodium.[31] At lower concentrations, the mean composition falls off sharply from the value 2.33 at the maximum to 1.2 at a concentration of 0.005 N. Bismuth and tin likewise form complexes of a similar nature which have not thus far been studied in detail.

The solutions of these complexes, except possibly at the highest concentrations, are purely electrolytic in character.[32] While the number of charges associated with the negative complex has not been definitely determined in the case of lead and antimony, it is probable that the charges are respectively 4 and 3, corresponding with the position of these elements in the periodic system. It is evident that many metallic elements are capable of forming complex anions similar to the complex sulphur and iodide ions. The compounds which are left behind on evaporation of ammonia are metallic. In view of the electrolytic properties of these compounds when in solution, it appears probable that the solid compounds themselves are, in fact, salt-like in character, the more electronegative element carrying a negative charge. The existence of a large number of compounds in binary systems, such as those of sodium and lead, is probably due to the formation of negative ionic complexes. In all likelihood, this property is not confined to the metals whose compounds are soluble in ammonia. It is probable that the constitution of the compounds formed between the strongly electropositive elements and such elements as thallium and mercury is similar to those of lead.

9. *Other Complex Ions.* Complex anions are formed by many salts of metallic and non-metallic elements on interaction with salts of the

[28] Kraus, *J. Am. Chem. Soc.* *29*, 1557 (1907); Smyth, *ibid.*, *39*, 1299 (1919).
[29] Peck, *J. Am. Chem. Soc.* *40*, 335 (1918).
[30] Smyth, *loc. cit.*
[31] Peck, *loc. cit.*
[32] Kraus, *J. Am. Chem. Soc.* *43*, 752 (1921).

more electropositive elements. Many such complex anions have been investigated in which mercury, tin, lead, platinum, silicon and other elements appear in the anion complex in association with strongly electronegative elements such as chlorine, fluorine, etc. The constitution of these complex anions is accounted for by Werner's theory which has already been briefly outlined.

Complex or, preferably, intermediate ions, both positive and negative, may be formed when salts of higher type ionize in stages. Such ions have many representatives among the higher types of weak acids and bases when the ionization constants of the different ions have different values. This is the case, for example, with phosphoric acid.

Whether similar complex ions are commonly formed in solutions of salts of higher type is uncertain. The cation transference number of cadmium iodide at high concentrations is greater than unity, which clearly indicates the existence of an intermediate cadmium ion. In the case of other salts, the existence of intermediate ions is not definitely established although, as we shall see below, the existence of such ions in mixtures may be inferred from solubility data. There are no data available relative to the existence of similar ions in non-aqueous solutions. It is possible, also, that binary electrolytes may associate and dissociate with the formation of complex ions. Their existence has not been established.

Chapter IX.

Homogeneous Ionic Equilibria.

1. *Equilibria in Mixtures of Electrolytes.* If the constituents in a mixture of two or more electrolytes obey the mass-action law, then the equilibrium in the mixture may at once be determined if the values of the mass-action constants are known. The values of these constants may in general be determined from a study of solutions of the pure substances under corresponding conditions. The equations underlying such equilibria have the form:

$$\frac{C^+C^-}{C_u} = K,$$

where C^+ denotes the concentration of the positive ions, C^- that of the negative ions, and C_u that of the un-ionized fraction of a given electrolyte. K is the ionization constant of the electrolyte in question. For every electrolyte appearing in the solution as an un-ionized molecule, the concentrations of its un-ionized fraction and of its ions appear as variables. In general, these ions will also be common to other electrolytes present in the mixture. The total number of ionic species in solution will be equal to the total number of un-ionized species in solution in case any number of electrolytes without a common ion are mixed. The mass-action law leads to a series of reaction equations of the type:

$$M_1^+ \times X_1^- = K_1 M_1 X_1,$$

and the concentrations of the various molecular species present in the solution, and to a series of condition equations of the type:

$$M_1X_1 + M_1X_2 + \ldots + M_1^+ = C_{M_1}$$
$$\text{and} \quad M_1X_1 + M_2X_1 + \ldots + X_1^- = C_{X_1}.$$

The number of equations will always be equal to the number of variables and the concentrations of the various molecular species present in the solution may be determined by solving the resulting simultaneous equations. If two electrolytes without an ion in common are mixed, the resulting reaction equations are:

$$M_1^+ \times X_1^- = K_1 M_1X_1$$
$$M_2^+ \times X_2^- = K_2 M_2X_2$$
$$M_2^+ \times X_1^- = K_3 M_2X_1$$
$$M_1^+ \times X_2^- = K_4 M_1X_2,$$

and the condition equations are:

$$M_1 + M_1X_1 + M_1X_2 = C_1$$
$$M_2 + M_2X_2 + M_2X_1 = C_2$$
$$X_1 + M_1X_1 + M_2X_1 = C_1$$
$$X_2 + M_1X_2 + M_2X_2 = C_2$$

where C_1 and C_2 are the total concentrations of the base M_1 or acid X_1, which are necessarily equivalent, and the base M_2 or the acid X_2, which are likewise equivalent. From these eight equations the concentrations of the eight different molecular species may be determined for any concentrations C_1 and C_2 of the total acids and the total bases in solution. In this case, interaction with the solvent is assumed not to take place. In a mixture of two electrolytes with a common ion we have the reaction equations:

$$M_1^+ \times X^- = K_1 M_1X$$
$$M_2^+ \times X^- = K_2 M_2X$$

and the condition equations:

$$M_1X + M_1 = C_1$$
$$M_2X + M_2 = C_2$$
$$M_1X + M_2X + X = C_1 + C_2.$$

In this case the solution of the problem is comparatively simple.

In a mixture of two electrolytes having an ion in common, assuming the mass-action law to hold, the ionization of the electrolytes in the mixture will be the same as that in the original solutions before mixing, if the concentrations of the common ion in these solutions, before mixing, are equal. Such solutions are said to be isohydric.[1] This result is a consequence of the law of mass-action. Let M_1^+, M_2^+ and X^- be the concentrations of two solutions having in common the ion X^-. It is obvious that the concentration of the common ion in these two solutions will be equal to M_1^+ for the first solution and M_2^+ for the second solution. Let a volume V_1 liters of the first solution be mixed with a volume of V_2 liters of the second solution. If the concentrations of the ion X^- in the two original solutions are equal, then we obviously have:

$$M_1^+ = M_2^+ = X^-.$$

[1] Arrhenius, *Ann. d. Phys. 30,* 51 (1887); *Ztschr. f. phys. Chem. 2,*284 (1888); *ibid.,* 5, 1 (1890).

In the mixture, therefore, assuming that no displacement of the equilibrium takes place, we should have for the concentration of the ions M_1^+ the value $\frac{M_1^+V_1}{V_1 + V_2}$, for that of the common ion $\frac{M_1^+V_1 + M_2^+V_2}{V_1 + V_2}$ and for that of the un-ionized fraction $M_1X_1\frac{V_1}{V_1 + V_2}$. If the law of mass-action holds, we have the equation:

$$\frac{\frac{M_1^+V_1}{V_1 + V_2} \times \frac{M_1^+V_2 + M_2^+V_2}{V_1 + V_2}}{M_1X_1 \frac{V_1}{V_1 + V_2}} = K_1.$$

If $M_1^+ = M_2^+$, the expression for the concentration of the common ion becomes:

$$\frac{M_1^+V_1 + M_1^+V_2}{V_1 + V_2} = M_1$$

and the equilibrium equation reduces to:

$$\frac{M_1^+ \times X_1^-}{M_1X_1} = K_1.$$

In other words, if the concentration of the common ion is the same in the original solutions, then, if these solutions are mixed in any proportion, assuming no change in the equilibrium to take place, the concentrations of the ions in the mixture will be such as to fulfill the conditions necessary for equilibrium.

The correctness of this principle may readily be tested in the case of weak acids. Since the conductance in solutions of the acids is due chiefly to the conductance of the hydrogen ion, it follows that two acids will have the same concentration of the hydrogen ion when the solutions have the same specific conductance. Therefore, a mixture of two solutions fulfilling these conditions will have the same specific conductance as the original solutions. If the anions have different conductance values, the specific conductance of isohydric solutions will differ in proportion to the conductance of these anions, and the specific conductance of a mixture of the solutions will be the arithmetic mean of that of the components. This principle has been extensively tested by the conductance as well as other methods and has been shown to hold true for mixtures of weak acids and bases.

It has been found, however, that even in solutions which do not conform to the law of mass-action, that is, in solutions of strong electrolytes,

a similar condition holds. If, for example, solutions of sodium chloride and potassium chloride have the same ion concentration, then, on mixing, the concentration of the ions in the mixture will be the same as that in the original solutions. Apparently, then, the isohydric principle holds, even in the case of electrolytes which do not obey the law of mass-action. This principle has been employed very extensively for the purpose of calculating the concentrations in mixtures of strong electrolytes. If the electrolytes in a given mixture do not obey the law of mass-action, then it is obviously impossible to calculate the equilibrium in the mixture unless we know the law governing this equilibrium. The isohydric principle is an empirical relation which has been assumed to govern the equilibrium in mixtures. In order to test the correctness of this principle, it is obviously necessary to determine the concentrations of the ions in the mixture by some independent means.

The law of equilibrium for a given electrolyte in a mixture must reduce in the limit to that of a solution of the electrolyte in the pure solvent. It has been shown that, for a strong electrolyte, Equation 11 holds very nearly. According to this equation, the ratio of the product of the concentrations of the ions divided by the concentration of the un-ionized fraction varies as an exponential function of the ion concentration. It is clear that this relation conforms to the principle of isohydric solutions. In a mixture of electrolytes, the equation might take the form:

$$\frac{P_i}{C_u} = D(\Sigma C_i)^m + K, \tag{50}$$

where P_i is the value of the ion product, C_u is the concentration of the un-ionized fraction, and C_i is the total concentration of the positive or negative ions in the mixture. Indeed, it is apparent that an equation of the form:

$$\frac{P_i}{C_u} = F(\Sigma C_i) \tag{51}$$

will conform to the isohydric principle,[1] where $F(\Sigma C_i)$ is any explicit function of the total ion concentration of the mixture. For, on mixing two solutions whose ion concentrations are C_i' and C_i'', the equilibrium will be unaffected by the relative volumes of the solutions mixed, pro-

[1] Arrhenius, *Ztschr. f. phys. Chem.* *31*, 218 (1899).

vided that C_i' and C_i'' are equal. Equation 51, therefore, is the analytical expression of the isohydric principle. In the limit, as the second component in the mixture disappears, the equation reduces to that for the first salt alone. In the case of mixtures of electrolytes without a common ion the same expression applies.

Equation 51 is not the only function which might be assumed to hold for the mixture which reduces to the form of Equation 11 in the case of a solution of a single electrolyte. We might assume for the mixtures a function of the form:

$$\frac{P_i}{C_u} = F(P_i), \tag{52}$$

where again P_i is the ion product. In the limit the concentrations of the positive and negative ions become equal for the solution of a single salt, and consequently this equation reduces to the form of Equation 11. The isohydric principle, or more generally, the iso-ionic principle, is a consequence of the law of mass-action, but, when the law of mass-action fails to hold, there is no reason for assuming that Equation 51 rather than Equation 52 is correct, for both reduce to the same limiting form in the case of a solution of a single electrolyte. We may, therefore, inquire which of the two functions corresponds most nearly with the experimental values.

In order to test the functions in the case of mixtures, it is obviously necessary to measure some property of these mixtures by independent means, as, for example, the conductance of a mixture of electrolytes. Assuming that the conductance of the ions in the mixture is the same as that of the same ions in pure solutions, it is possible to calculate the specific conductance of the mixture, if the form of the conductance function for the pure electrolytes is known, and if a function is assumed for the mixture. If the assumed function is correct, then the calculated specific conductance for the mixture should correspond to the measured specific conductance of the mixture within the limits of experimental error. If the calculated and observed values do not correspond, it follows that the function assumed for the mixture is not correct. That an equilibrium actually exists in the mixture appears to be beyond question, although the exact nature of the reaction may be somewhat in doubt.

Bray and Hunt[2] have measured the specific conductance of mixtures of sodium chloride and hydrochloric acid in water at 25°. They have likewise calculated the specific conductance of the mixtures, assuming

[2] Bray and Hunt, *J. Am. Chem. Soc.* 33, 781 (1911).

the isohydric principle; that is, assuming Equation 51. The results are given in Table LXXXIII, in which the concentrations of sodium chloride and hydrochloric acid are given in the second and third columns respectively, and the measured specific conductance is given in the fourth column. In the fifth column is given the specific conductance calculated on the assumption of the iso-ionic principle, namely Equation 51, while in the seventh column is given the value of the calculated specific conductance, assuming Equation 52. In the sixth and eighth columns are given the percentage deviations between the measured and calculated values.

TABLE LXXXIII.

Measured Specific Conductance of Mixtures of NaCl and HCl Compared with Values Calculated According to Equations 51 and 52.

	Concentration (Approx.) millimols		Specific Conductance μ				
No.	NaCl	HCl	Measured	Calculated Equation 51	% Dif.	Calculated Equation 52	% Dif.
1	100	100	47.25	48.21	—2.1	47.09	+0.3
2	100	50	29.14	29.62	—1.6	28.82	+1.1
3	100	20	18.06	18.31	—1.4	17.84	+1.2
4	100	10	14.36	14.50	—1.0	14.18	+1.2
5	100	5	12.52	12.59	—0.6	12.39	+1.1
6	100	2	11.41	11.45	—0.3	11.35	+0.5
				Mean	—1.15%	Mean	+0.85%
7	20	50	21.75	21.89	—0.7	21.65	+0.4
8	20	20	10.157	10.27	—1.1	10.13	+0.3
9	20	10	6.253	6.307	—0.9	6.221	+0.5
10	20	4	3.889	3.919	—0.8	3.870	+0.3
11	20	2	3.101	3.118	—0.6	3.094	+0.2
12	20	1	2.709	2.721	—0.4	2.702	+0.3
				Mean	—0.75%	Mean	+0.33%
13	5	12.5	5.651	5.678	—0.5	5.646	+0.1
14	5	5	2.632	2.650	—0.7	2.634	—0.1
15	5	2	1.621	1.630	—0.6	1.619	+0.1
16	5	1	1.011	1.016	—0.5	1.010	+0.1
				Mean	—0.57%	Mean	+0.05%

Comparing the measured values of the specific conductance with those calculated on the basis of Equation 51, it is seen that the deviations from the iso-ionic principle are consistently larger than any conceivable experimental error. In the case of 0.1 normal solutions of sodium chloride, the

mean error is 1.15 per cent; for 0.02 normal solutions, 0.75 per cent; and for 0.005 normal sodium chloride solutions, the mean deviation is 0.57 per cent. At the lower concentrations the agreement is measurably better than at the higher concentrations, a result which is perhaps not unexpected, since at concentrations as high as 0.1 normal viscosity effects unquestionably come into play. The agreement between the measured and calculated values based on Equation 52 is markedly better than that of values based on Equation 51. In the case of the 0.1 normal solutions of sodium chloride, the mean deviation is 0.85 per cent. In the mixtures of sodium chloride of concentration 0.02 and 0.005, the mean deviations are respectively 0.33 and 0.05 per cent, values which fall very nearly within the limits of experimental error. In calculating the specific conductances of the mixtures according to Equation 52, 424 was assumed for the value of Λ_0 for hydrochloric acid and 127 for that of sodium chloride. These values may be somewhat in error, but it is to be noted that the calculated specific conductances are affected to only a very small extent by the value assumed for Λ_0. It must be concluded from these results that the isohydric principle is not applicable to mixtures of strong electrolytes. In the case of the mixtures of hydrochloric acid and sodium chloride, at any rate, Equation 52 yields results which correspond quite closely with the observed values at low concentrations. It is uncertain, however, that a similar correspondence will be found in the case of mixtures of other electrolytes. For the present, therefore, the form of the function which should be assumed in the case of mixtures of strong electrolytes remains doubtful.

2. *Hydrolytic Equilibria.* Water itself is ionized to a slight extent into hydrogen and hydroxyl ions. There therefore exists in water an equilibrium which, if the law of mass-action holds, is expressed by the equation:

$$H^+ \times OH^- = K_w,$$

where K_w is the ionization constant of water. The concentration of the hydrogen and hydroxyl ions in pure water has been determined by Kohlrausch from the conductance of very pure water. At 18° this method yielded the value 0.80×10^{-7} for the concentration of the hydrogen and hydroxyl ions in pure water. The ionization constant has also been determined from the electromotive force of gas cells, from the rate of certain esterrification reactions and from the hydrolysis of certain salts in water. In these latter methods, an electrolyte has, in general, been present, which naturally introduces an uncertainty as to the effect of

the electrolyte on the ionization constant of water. The results of the various methods are summarized in the following table.

TABLE LXXXIV.

THE HYDROGEN-ION CONCENTRATION ($\times 10^7$) IN PURE WATER AS DETERMINED BY VARIOUS INVESTIGATORS.

Investigator	Method of Determination	0°	18°	25°
Arrhenius	Hydrolysis of sodium acetate by ester-saponification	...	...	1.1
Wijs	Catalysis of ester by pure water..	...	...	1.2
Nernst	Electromotive force of gas cell...	...	0.8	...
Löwenherz	Electromotive force of gas cell...	...	...	1.19
Kohlrausch and Heydweiller ..	Conductance of pure water.......	0.36	0.80	1.06
Kanolt	Hydrolysis	0.30	0.68	0.91

When a salt is dissolved in water, interaction takes place between the ions of the salt and the ions of water with the resultant formation of un-ionized molecules of acid, or of base or of both, depending upon the strength of the acid and the base. Assuming the law of mass-action to hold in the mixture for both acid and base, and assuming that the salt is highly ionized and that its ionization function is known and is the same in the mixture as it is in a solution of the salt alone, the concentration of the various constituents in the mixture may be obtained from a solution of the reaction equations:

$$
\begin{aligned}
&H^+ \times X^- = K_a HX,\\
(53)\qquad &M^+ \times OH^- = K_b MOH,\\
&H^+ \times OH^- = K_w,
\end{aligned}
$$

and the condition equations:

$$
\begin{aligned}
&MX + HX + X^- = C_a,\\
(54)\qquad &MX + MOH + M^+ = C_b,\\
&M^+ + H^+ = X^- + OH^-,
\end{aligned}
$$

where K_a, K_b and K_w are the ionization constants of acid, base, and water, respectively, and C_a and C_b are the total concentrations of acid and of base, and the other symbols represent the concentrations of the various constituents concerned in the reaction. Let us assume that the acid is stronger than the base, in which case H^+ is greater than OH^-. Let γ_s represent the fraction of base present in the form of ions. Since

M^+ differs from X^-, γ_s is not identical with the ionization of the salt, but, unless the hydrolysis is great, the value of γ_s will not differ appreciably from that of the salt at the concentration in question. Let h represent the total fraction of base present in the un-ionized condition, in which case h is the hydrolysis coefficient. A solution of the above equations leads to the equation:

$$(55) \qquad \frac{K_w\gamma_s(1-h)}{K_bh}\left[\gamma_sC_b(1-h)+\frac{K_w\gamma_s(1-h)}{K_bh}-\frac{K_bh}{\gamma_s(1-h)}\right]=$$
$$K_a\left[(C_a-C_b+hC_b-\frac{K_w\gamma_s(1-h)}{K_bh}+\frac{K_bh}{\gamma_s(1-h)}\right].$$

The concentrations of the various constituents are given by the following equations:

$$HX=C_a-C_b+hC_b-\frac{K_w\gamma_s(1-h)}{K_bh}-\frac{K_bh}{\gamma_s(1-h)}$$
$$X^-=\gamma_sC_b(1-h)+\frac{K_w\gamma_s(1-h)}{K_bh}-\frac{K_bh}{\gamma_s(1-h)}.$$
$$(56) \qquad OH^-=\frac{K_bh}{\gamma_s(1-h)}$$
$$H^+=\frac{K_w\gamma_s(1-h)}{K_bh}$$
$$M^+=\gamma_sC_b(1-h)$$
$$MOH=hC_b$$

If γ_s, together with the reaction constants, are known, the concentrations of the constituents may be calculated. The equations may be generalized by introducing the ionization function K_s for the salt by means of the equation:

$$(57) \qquad M^+\times X^-=K_sMX.$$

This leads to the equation:

$$(58) \qquad \gamma_s\left[\gamma_sC_b(1-h)+\frac{K_w\gamma_s(1-h)}{K_bh}-\frac{K_bh}{\gamma_s(1-h)}\right]=K_s(1-\gamma_s).$$

These equations are independent of the concentration of the various reacting constituents so long as the assumed conditions are fulfilled. In many instances they may be greatly simplified for practical purposes. If the concentration of the salt is not extremely low and if the acid is stronger than the base, the concentration of the hydroxyl ions may be neglected in comparison with that of the M^+ ions, and the term $\frac{K_b h}{\gamma_s (1-h)}$ may be dropped out of the equations. If the hydrolysis is small, the concentration of the hydrogen ions may be neglected in comparison with that of the M^+ ions. The equation, then, reduces to the form:

$$\frac{h^2}{(1-h)^2} = \frac{K_w \gamma_s^2}{K_a K_b} - \frac{C_a - C_b}{C_b} \frac{h}{(1-h)^2} + \frac{K_w}{K_b} \frac{\gamma_s}{C_b (1-h)}. \tag{59}$$

If acid and base are present in equivalent amounts, the hydrolysis of the salt is expressed by the equation:

$$\frac{h^2}{(1-h)^2} = \frac{K_w \gamma_s^2}{K_a K_b} + \frac{K_w \gamma_s}{K_b C_b (1-h)} \tag{60}$$

and the hydrogen ion concentration by:

$$H^{+2} = \frac{1}{\frac{K_b}{K_w K_a} + \frac{K_b}{K_w \gamma_s C_b (1-h)}}. \tag{61}$$

These equations are generally applicable, provided the concentration of the hydrogen ions is relatively small in comparison with that of the ions of the salt. In the case of a solution of a strong acid and a weak base, the second term in Equation 60 is evidently determinative of the degree of hydrolysis of the salt, while in solutions in which both the acid and base are very weak and the total concentration of the base is high, the first term is chiefly determinative of the hydrolysis. In the case of acids and bases of intermediate strength, and particularly at fairly low concentrations, both terms must be taken into account in determining the hydrolysis of a salt.

In very dilute solutions of salts of relatively strong acids and bases, it is possible that conductance measurements may be appreciably affected by hydrolysis. This is particularly true if the limiting values of the ionization constant approached by acid and base differ. It is obvious that the actual concentration of acid and of base in solution is very low,

and the values of the ionization functions to be introduced for acid and base are therefore not the values for these ionization functions at ordinary concentrations of acid and base, but rather the values approached at very low concentrations. Actually, we do not know the limiting value which the ionization functions approach in aqueous solutions of strong acids and bases. Consequently, conductance measurements with dilute salt solutions remain in doubt so long as the values of the ionization functions remain unknown. It is fairly certain that in the case of salts of weaker bases, such as the silver salts, for example, the conductance must be measurably affected at concentrations below 10^{-3} normal. According to Böttger,[3] the ionization constant of silver oxide at 25° is 2.5×10^{-4}. Assuming for the ionization constant of water the value 0.91×10^{-14} and assuming that the ionization of the salt is practically complete, we obtain the following values for the hydrolysis of silver salts at 25°.

TABLE LXXXV.

HYDROLYSIS OF SILVER SALTS AT DIFFERENT CONCENTRATIONS AT 25°.

C	10^{-3}	10^{-4}	10^{-5}
h	1.9×10^{-4}	6.0×10^{-4}	1.9×10^{-4}
Cond. inc.	5.7×10^{-4}	1.8×10^{-3}	5.7×10^{-3}

As a result of the replacement of Ag^+ ions by H^+ ions in the solution, the conductance is increased approximately in the ratio of one to three. In the third line of the above table are given values of the increase in the conductance due to the hydrolysis of the salt. It is seen that even at 10^{-3} normal the conductance of a silver salt is affected to the extent of 0.057%, while in a 10^{-4} normal solution the conductance correction amounts to 0.18%. That the hydrolysis of salts of the weaker bases becomes appreciable at higher temperatures is indicated by the work of Noyes and Melcher[4] with the salts of silver and of barium. In the case of silver nitrate, at higher temperatures, a deposit of silver was formed over the inner walls of the platinum-lined bomb. This presumably was the result of a precipitation of silver oxide, which is unstable at these temperatures and decomposes to metallic silver and oxygen.

The extent of the hydrolysis of salts of strong acids and bases is very uncertain. At the higher concentrations, these electrolytes appear to be ionized somewhat more strongly than typical salts. Washburn has deduced the value of 0.02 as the limit approached by the ionization constant of potassium chloride at low concentrations. But this value really

[3] Böttger, *Ztschr. f. phys. Chem.* 46, 602 (1903).
[4] Noyes, Carnegie Publication, No. 63, p. 94.

represents an upper limit and it is possible that the true value may be much below this limit. The high value of the ionization, however, renders any precise determination of the limiting value of the mass-action function uncertain, and, indeed, if conductance data alone are considered it is even uncertain that a definite limit greater than zero is approached.[4a] The strong acids and strong bases are ionized to practically the same extent at higher concentration; and if the ionization functions in the case of these two types of electrolytes approach the same limits at low concentrations, the conductance of a salt as measured will be found somewhat lower than the true value if hydrolysis becomes appreciable. On the other hand, if the functions of acid and of base approach values which differ considerably, then the result will be to increase the conductance of the solution above that of the unhydrolyzed salt. If, for example, the ionization constant of the acid relative to that of the base were 10^{-3}, then, at a salt concentration of 10^{-5} N, the hydrolysis would have a value of 0.95×10^{-3} or approximately 0.1 per cent, which would raise the conductance of the solution approximately 0.3 per cent. In view of the entire lack of experimental data relating to the limiting values of the ionization constants of the strong acids and bases, conductance measurements with salts at concentrations below 10^{-4} normal cannot be interpreted with certainty.

In solutions of salts of weaker acids and bases, hydrolytic equilibria appear to be fairly well established. This lends support to the view that the ionization constants of the weaker acids and bases, as well as that of water, are not materially affected by the presence of larger amounts of salt. The agreement of the values for the ionization constant of water as determined from a measurement of the conductance of solutions of salts of weak acids and bases, with that as determined by other methods, indicates that the fundamental assumptions underlying the theory of hydrolytic equilibria are substantially correct. In these equilibria, the ionization of the salt is involved. If, as some assume, the salts are completely ionized at all concentrations, then the ionization γ_s of the salt should vanish from the hydrolysis equation, which would materially affect the values obtained for the ionization constant of water. At the present time, however, data making such a comparison possible are not sufficiently precise to enable us to draw any certain conclusions.

Among other typical equilibria involving electrolytes are those in which a strong acid or a strong base is partitioned between two weaker

[4a] Naturally, if this view were adopted, it would be necessary to recast our notions relative to the nature of electrolytic equilibria.

bases or weaker acids.[5] A considerable number of equilibria of this type have been investigated and, in general, the results confirm the assumption that the strong base or acid is distributed between the weaker acids or bases in conformity with the law of mass-actión.

Equilibria similar to hydrolytic equilibria in aqueous solutions have been found to exist in solutions in non-aqueous solvents. Such equilibria are to be expected in the case of all distinctly acid solvents which are capable of yielding a hydrogen ion. This, therefore, includes solutions in all acids, such as hydrocyanic acid, formic acid, acetic acid, etc. It likewise includes solutions in hydrogen derivatives whose acid properties are extremely weak, such as ammonia, for example.

Franklin[6] has shown that equilibria of the hydrolytic type exist in solutions in liquid ammonia. In the case of salts of very weak bases, such as mercury for example, ammono-basic salts are precipitated when the neutral salt is dissolved. These precipitates are redissolved on the addition of an acid, while precipitation is facilitated by the addition of an ammono-base, such as potassium amide. While equilibria of the hydrolytic type thus exist in ammonia solutions, the evidence indicates that it is only in the case of extremely weak bases that hydrolysis takes place to an appreciable extent. The concentration of hydrogen ions in ammonia is without doubt of an exceedingly low order. This is indicated by the fact that salts whose ammono-bases are practically insoluble in liquid ammonia, such as calcium and barium nitrates, for example, yield clear solutions when dissolved in ammonia, even at high concentrations. Furthermore, as is well known, solutions of the alkali metals, as well as of metals of the alkaline earths, in liquid ammonia, are comparatively stable. It is to be expected that such would not be the case if the concentration of the hydrogen ions were appreciable.

Schlesinger[7] has shown that solutions of salts in formic acid are appreciably hydrolyzed. He found that on passing a current of air through solutions of chlorides in formic acid free hydrochloric acid is carried over. That hydrolysis may occur in solutions in other solvents, such as hydrocyanic acid, for example, is indicated by the high value of the residual specific conductance of the pure solvents. It is, of course, possible that in these cases the conductance is in a measurable degree due to the presence of impurities, but the high value obtained in many instances is probably due to the presence of hydrogen ions. It is probable, moreover, that the higher the dielectric constant of the medium, the greater the concentration of hydrogen ions due to the solvent. No

[5] Thiel and Roemer, *Ztschr. f. phys. Chem. 61*, 114 (1908).
[6] Franklin, *J. Am. Chem. Soc. 27*, 820 (1905).
[7] Schlesinger, *J. Am. Chem. Soc. 33*, 1932 (1911).

systematic study has been made of reactions of the hydrolytic type in non-aqueous solvents.

Certain solvents, such as sulphur dioxide, acetone and bromine, for example, appear to be of a non-polar type. In these cases it is to be expected that equilibria of the hydrolytic type do not exist. In the case of polar solvents, however, we may expect equilibria of the hydrolytic type even though hydrogen ions are not involved. Mercuric chloride may serve as an example of this type of solvents. This salt, when fused, dissolves typical binary salts and yields solutions which conduct the current with considerable facility. If a salt of the type of potassium nitrate, for example, were dissolved in mercuric chloride, reaction might be expected to take place, with the formation of potassium chloride and mercuric nitrate in the solution. This reaction is obviously of the hydrolytic type. Indeed, we see that reactions of the type $MX + NY = NX + MY$, which take place in mixtures of fused salts, are of the hydrolytic type. We have here, however, an extreme case in that, in all likelihood, the ionization of the solvent itself is extremely high, whereas in the case of ordinary hydrolytic reactions the ionization of the solvent is exceedingly low. There is reason for believing that examples exist of equilibria of the hydrolytic type intermediate between those of water and those of mixtures of fused salts.

Chapter X.

Heterogeneous Equilibria in Which Electrolytes Are Involved.

1. *The Apparent Molecular Weight of Electrolytes in Aqueous Solution.* If an electrolyte is dissolved in a solvent in equilibrium with a second phase, the thermodynamic potential of the solvent is displaced, and a displacement in equilibrium results. On the addition of an electrolyte to water, therefore, we should expect a change in the solubility of substances in this solvent; or, in case water itself appears as a second phase, we should expect a displacement in the freezing point, boiling point, etc.

The earlier experiments on the freezing point of aqueous salt solutions indicated a fairly close agreement between the ionization as determined by conductance measurements and that as determined from freezing point measurements. These data have been examined and collected by Noyes and Falk.[1] In solutions of the binary salts the agreement is, on the whole, fairly close in dilute solutions, although in the more concentrated solutions deviations, which exceed possible experimental errors, make their appearance. In solutions of potassium chloride the two methods yield practically identical results up to concentrations as high as 0.1 normal.

In order to calculate the molecular weight of a substance from the freezing point of its solution, the laws governing the equilibrium in the mixture must be known. Since the general case has been worked out only for dilute solutions, it is obvious that the ionization of electrolytes, and the molecular condition of substances in general, may not be determined from freezing point determinations at higher concentrations. Washburn and MacInnes[2] showed that, while the freezing point curve for potassium chloride corresponds very nearly with that of a solution of sugar in water up to fairly high concentrations, those for solutions of lithium chloride and caesium nitrate exhibit deviations at fairly high dilutions. The deviations in the case of the last named salts lie in opposite directions from the theoretical curve of ideal solutions. They found,

[1] Noyes and Falk, *J. Am. Chem. Soc.* *33*, 1437 (1911).
[2] Washburn and MacInnes, *J. Am. Chem. Soc.* *33*, 1686 (1911).

however, that at lower concentrations the curves for the three salts approach that of an ideal system, assuming the ionization to be given by the conductance ratio $\frac{\Lambda}{\Lambda_0}$.

More recently the methods for determining the temperature of solutions in equilibrium with ice have been greatly refined, and molecular weight determinations are available at very low concentrations. In Table LXXXVI, under γ_i are given values of the ionization for potassium chloride at low concentrations as determined by Adams[3] and by Bedford.[4] Under γ_c are given values of the ionization at the same concentrations as determined from conductance measurements.

TABLE LXXXVI.

COMPARISON OF THE IONIZATION VALUES FOR POTASSIUM CHLORIDE FROM FREEZING POINT AND CONDUCTANCE MEASUREMENTS.

$C \times 10^3$	γ_i (Adams)	γ_i (Bedford)	γ_c
2	0.969	....	0.971
5	0.961	0.959	0.956
10	0.943	0.939	0.941
20	0.922	0.915	0.922
50	0.888	....	0.889
100	0.861	....	0.860

An examination of this table shows that the ionization values as determined by the freezing point method correspond within the limits of error with those as determined by the conductance method. The temperature of the conductance measurements, in this case, was 18°, while that of the freezing point measurements was necessarily in the neighborhood of 0°. It is known, however, that at fairly high dilutions the ionization of salts varies only little between 0° and 18°. The results are therefore comparable.

In Table LXXXVII are given values of the ionization as determined from freezing point and conductance measurements for solutions of potassium nitrate, potassium iodate, sodium iodate, and for equi-molar mixtures of potassium chloride and potassium nitrate, and potassium iodate and sodium iodate.[5]

Examining the results given in the following table, it is evident that, in the case of potassium nitrate, the ionization values by the two methods

[3] Adams, *J. Am. Chem. Soc.* *37*, 482 (1915).
[4] Bedford, *Proc. Roy. Soc.* (A) *83*, 454 (1910).
[5] Hall and Harkins, *J. Am. Chem. Soc.* *38*, 2658 (1916).

TABLE LXXXVII.

COMPARISON OF THE IONIZATION VALUES OF SALTS AS DERIVED FROM FREEZING POINT AND CONDUCTANCE MEASUREMENTS.

Potassium Nitrate

$C \times 10^3$	γ_i (Adams)	γ_c
2	0.967	0.970
5	0.958	0.953
10	0.937	0.935
20	0.908	0.911
50	0.848	0.867
100	0.787	0.824

Potassium Iodate

$C \times 10^3$	γ_i (Hall & Harkins)	γ_c
2	0.940	0.965
5	0.929	0.946
10	0.916	0.928
20	0.890	0.903
50	0.835	0.860
100	0.764	0.819

Sodium Iodate

$C \times 10^3$	γ_i (Hall & Harkins)	γ_c
2	0.950	0.960
5	0.934	0.939
10	0.915	0.917
20	0.890	0.890
50	0.832	0.842
100	0.772	0.801

Equal Molecular Mixtures of KCl and KNO_3

$C \times 10^3$	γ_i (Hall & Harkins)
10	1.94
20	1.914
50	1.868
100	1.827
200	1.773

Equal Molar Mixtures of KIO_3 and $NaIO_3$

$C \times 10^3$	γ_i (Hall & Harkins)
10	1.912
20	1.890
50	1.834
100	1.768

agree at concentrations below 20×10^{-3} N. At higher concentrations, however, the freezing point method yields lower values than the conductance method. In the case of potassium iodate, the agreement is not so good. At the lower concentrations the value of the ionization as determined by the conductance methods is about 1.5 per cent higher than that determined by the freezing point method. The limiting value of the conductance of the iodates'is much less certain than is that of the chlorides and nitrates, and it is possible that the ionization values, as determined by this method are in error owing to an error in the value of Λ_0. If the value of Λ_0 were increased by 1.5 per cent, the conductance values for potassium iodate would agree up to a concentration of 0.05 normal. In solutions of sodium iodate, the discrepancies exceed the limit of experimental error, of the conductance measurements, at any rate. It is possible that here, also, an error in the value of Λ_0 would tend to harmonize the results.

As regards the freezing point of equi-molar mixtures of two electrolytes, it is interesting to note that the values of i for the mixtures are practically the mean of those for the pure substances at the same concentration.

In Table LXXXVIII are given values of i for salts of higher type,[6] together with values of γ_i and γ_c, where reliable values of γ_c are available.

TABLE LXXXVIII.

IONIZATION OF SALTS OF HIGHER TYPE AS DETERMINED BY THE FREEZING POINT AND CONDUCTANCE METHODS.

$C\times10^3$	i (Hall & Harkins)	γ_i (Hall & Harkins)	γ_c
	Magnesium Sulphate, $MgSO_4$		
5	1.708	0.708	0.741
10	1.614	0.614	0.669
20	1.520	0.520	0.596
50	1.394	0.394	0.506
100	1.303	0.303	0.449
200	1.214	0.214	0.403
500	1.099	0.099	.....
	Potassium Sulphate, K_2SO_4		
5	2.830	0.915	0.905
10	2.772	0.886	0.872
20	2.701	0.851	0.832
50	2.567	0.784	0.771
100	2.451	0.726	0.722
200	2.327	0.664	0.673

[6] Hall and Harkins, *loc. cit.*

Barium Chloride, $BaCl_2$

5	2.847	0.924	.....
10	2.790	0.895	0.883
20	2.730	0.865	0.850
50	2.647	0.824	0.798
100	2.585	0.793	0.759
200	2.535	0.768	0.720

Cobalt Chloride, $CoCl_2$

5	2.858	0.929
10	2.802	0.901
20	2.749	0.875
50	2.687	0.844

Lanthanum Nitrate, $La(NO_3)_3$

5	3.694	0.898	.....
10	3.578	0.859	0.802
20	3.440	0.813	.....
50	3.261	0.754	0.701
100	3.149	0.716	.....
200	3.063	0.688	.....
500	3.002	0.667	.....

The agreement between the ionization values as determined from conductance and freezing point measurements, in the case of the salts of higher type, is not as close as in that of the binary salts. The deviations in the more dilute solutions are in the neighborhood of one per cent, for the uni-divalent salts. In solutions of potassium sulphate the ionization values by the freezing point method are slightly higher than those by the conductance method, except at a concentration of 0.2 normal, where the conductance method gives a slightly higher value. On the whole, for this salt the agreement is fairly close and it is possible that the discrepancies which remain may be due to error in the value of Λ_0 employed. In the case of barium chloride, the ionization values by the freezing point method at the lower concentrations are slightly over one per cent higher than those by the conductance method. At the higher concentration the difference in the values increases to five per cent at 0.2 normal. The differences at the lower concentrations may arise from uncertainties in the values of Λ_0, but at the higher concentrations there is evidently a definite divergence between the two curves. Accurate conductance values for cobalt chloride are not available. The values of i, however, do not differ greatly from those of barium chloride or potassium sulphate.

In solutions of lanthanum nitrate, the ionization values as deter-

mined by the freezing point method are approximately seven per cent greater than those determined by the conductance method. Comparison, however, can be made only at two concentrations. The discrepancies in the values appear to be greater than might be expected from any possible errors in the assumed value of Λ_0. In the case of magnesium sulphate, there is a marked divergence between the values of the ionization as determined by the two methods. However, as the concentration decreases, the ionization curves, as given by the two methods, approach each other.

Considering these results broadly, it may be concluded that the freezing point and the conductance methods give values for the ionization which fall very nearly within the limits of experimental error at concentrations approaching 10^{-3} normal for solutions of the binary salts, and that in the case of solutions of salts of higher type the differences between the values, as determined by the two methods, do not, in general, exceed one per cent at low concentrations for salts of the uni-divalent type. For salts of the di-divalent type, the discrepancies between the values, as determined by the two methods, are markedly greater, lying in the neighborhood of 5 per cent, and the same is true of lanthanum nitrate. In general, however, in the case of salts of higher type, the divergence of the values determined by the two methods diminishes as the concentration decreases.

Considering the results of freezing point determinations, it is a striking fact, the significance of which cannot be ignored, that, as the concentration decreases, the molecular depression of the freezing point increases and approaches a limiting value, which, in the case of salts of different types, corresponds with the ionic structure of these salts and which is in agreement with the fundamental ionic reactions assumed by the ionic theory. So the value of i for the binary salts approaches a value of 2, for ternary salts 3, for quaternary salts 4, etc. While the significance of the agreement between the results of freezing point and conductance measurements remains uncertain, the fundamental importance of the fact that the limits approached in the two cases are substantially the same should not be overlooked.

The difference between the results by the two methods at the higher concentrations are readily explainable, since the calculation of the number of molecules present in a mixture is based upon the assumption that the laws of dilute solutions hold. Even in the case of non-electrolytes, the laws of dilute solutions fail to hold at concentrations as low as 0.1 normal, and it is therefore *a priori* probable that the laws of dilute solu-

of 16 liters, a few salts have a value of i greater than unity, while the greater proportion of the salts has a value of i less than unity. At higher concentrations the curves exhibit a very complex form. In the case of most of the substances which have a relatively high value of i at lower concentrations, the value changes but little until a concentration of 0.2 normal is reached, when the value of i begins to increase rapidly with increasing concentration. In the case of salts having a low value of i at the lower concentrations, the value of i, in general, decreases with increasing concentration, particularly as normal concentration is approached. Certain of the electrolytes exhibit an exceptional behavior in that the curves of the i values intersect those of the majority of the electrolytes. It is evident that molecular weight determinations in sulphur dioxide are uncertain in their significance. On the whole, the curves exhibit a definite trend as the concentration decreases indicating that the value of i will ultimately rise above unity. It is to be borne in mind that the ionization of salts in sulphur dioxide is relatively low, being in general less than 20 per cent in the neighborhood of 0.1 normal. Furthermore, even in the case of aqueous solutions, freezing point and conductance methods lead to divergent results at higher concentrations. If the divergence of a solution of an electrolyte from the simple laws of dilute solutions is in any considerable measure due to the electrostatic action of the charged particles upon one another or upon the solvent medium, then it is to be expected that as the dielectric constant of the solvent is smaller, the divergence at a given concentration will be greater, since the force due to a charged particle varies inversely as the dielectric constant. It seems not improbable, also, that, in the case of certain solvents, polymerization may take place to a considerable extent at higher concentrations. This would greatly complicate the behavior of these solutions and would make it impossible to interpret either the results of conductance or of osmotic measurements.

The molecular weights of a number of electrolytes in liquid ammonia at its boiling point have been determined by Franklin and Kraus[10] from the boiling point measurements. Owing to the exceptionally low value of the boiling point constant of liquid ammonia, about 3.4, measurements below 0.1 normal were not made. As a consequence, the determinations relate almost entirely to concentrations at which it might be expected that the laws of dilute solutions would not hold. In general, in the neighborhood of 0.1 normal, the observed elevation of the boiling point corresponds approximately with a normal value of the molecular weight of the dissolved electrolyte. At higher concentrations, the molecular eleva-

[10] Franklin and Kraus, *Am. Chem. J.* *20*, 836 (1898).

tion of the boiling point increases in the case of all the salts measured. It is obvious that in these solvents the concentration at which the measurements were carried out is too high to admit of a comparison with the results of the conductance method. In comparing the results of the conductance method with that of other methods of determining the degree of ionization of salts in non-aqueous solvents, it should be borne in mind that, according to conductance measurements, the deviations from the law of simple mass-action increase greatly as the dielectric constant of the medium decreases. If, then, the deviations from the laws of dilute solutions lead to a lack of correspondence between the results of the osmotic and the conductance methods, the discrepancy between the results of the two methods should be the greater, the greater these deviations. It might be expected, therefore, that, in solvents of low dielectric constant, the discrepancies would prove to be very great.

In solvents of fairly high dielectric constant, molecular weight determinations by osmotic methods yield values for the ionization which are comparable with those resulting from conductance measurements, and the ionization increases as the concentration decreases. In making such comparisons, however, it should be borne in mind, not only that the experimental errors are great in the osmotic determinations, but, also, that the conductance values are more or less uncertain, and that the values of Λ_0 are often subject to considerable errors. In the following table are given values of the ionization γ_c as determined from conductance measurements and γ_b as determined from the elevation of the boiling point for solutions of $(C_2H_5)_4NI$ in a number of solvents.[11]

TABLE XC.

VALUES OF *i* FOR SOLUTIONS IN DIFFERENT SOLVENTS.

CH_3OH			
V	3	6	12
γ_c	0.38	0.45	0.52
γ_b	0.24	0.29	0.38

CH_3CN		
V	10	15
γ_c	0.48	0.54
γ_b	0.49	0.57

C_2H_5OH	
V	30
γ_c	0.41
γ_b	0.30

C_2H_5CN	
V	30
γ_c	0.53
γ_b	0.54

[11] Walden, *Ztschr. f. phys. Chem.* 55, 281 (1906).

While the correspondence between the two methods is not very exact, nevertheless it is evident that the relations in these solvents are similar to those found in aqueous solutions.

In pyridine the values of i are in general less than unity, as may be seen from the following table.

TABLE XCI.

VALUES OF i FOR SOLUTIONS IN PYRIDINE.

	$AgNO_3$				$(C_2H_5)_4NI$	
$V=$	1	2	8	$V=$	16	32
$i=$	0.77	0.75	0.91	$i=$	0.73	0.82

The molecular weight of sodium iodide in acetone has been determined by McBain and Coleman.[12] The values obtained are very nearly normal from 0.9 to 0.04 normal concentrations. If anything, the molecular weights are slightly larger at the lower concentrations. At these concentrations, the conductance method indicates an ionization varying from 17 to 43 per cent. It is evident that in this solvent the results of conductance and of osmotic measurements are not in agreement. In acetone, however, the deviations from the law of simple mass-action are large, and there is evidence that polymerization of the dissolved salts takes place, presumably with the formation of complex ions.[12a] This renders the interpretation of results in the more concentrated solutions difficult.

Phenol is the only non-aqueous solvent in which the molecular weights of salts have been determined at relatively low concentration. Riesenfeld,[13] from the freezing point of a saturated solution of potassium iodide in phenol, whose concentration is 0.0045 normal, obtained a value of 170, for the molecular weight of potassium iodide, which corresponds closely with the normal value of 166. The equivalent conductance of solutions of potassium iodide in phenol at these concentrations is of the order of 1.0. Hartung[14] has measured the molecular weights of a number of salts in phenol by the freezing point method. These include tetramethylammonium iodide, sodium acetate, aniline hydrochloride, dimethylamine hydrochloride, as well as several organic salts of alkali metals. The concentrations run to dilutions, in some cases, as low as 0.01 normal. In the following table are given the values obtained for i for solutions of tetramethylammonium iodide and sodium acetate in phenol. With aniline hydrochloride, i has a value of unity at a concentration of 0.02 N

[12] McBain and Coleman, *Trans. Faraday Soc.* *15*, 45 (1919).
[12a] Serkov, *Ztschr. f. phys. Chem.* *73*, 567 (1910).
[13] Riesenfeld, *Ztschr. f. phys. Chem.* *41*, 346 (1902).
[14] Hartung, *Ztschr. f. phys. Chem.* *77*, 82 (1911).

and decreases to values less than unity at higher concentrations. In the case of dimethylamine hydrochloride i has a value of 1.18 at $V = 23$, and decreases to a value in the neighborhood of unity at a dilution of

TABLE XCII.

MOLECULAR WEIGHTS OF SALTS IN PHENOL.

Tetramethylammonium Iodide. $M = 201.1$

V	M(obs.)	i
92.7	135.5	1.48
38.9	143.5	1.40
22.9	150.2	1.34
12.3	163.9	1.23
8.18	171.5	1.17
5.70	177.6	1.13
4.75	182.6	1.10
4.08	185.4	1.08
3.52	188.8	1.07
3.05	189.0	1.06
2.67	190.0	1.05
2.40	191.1	1.05
2.10	191.5	1.06
1.73	188.9	1.07
1.59	185.3	1.08

Sodium Acetate. $M = 82.1$

V	M(obs.)	i
41.8	46.6	1.75
29.5	48.8	1.66
20.5	54.0	1.51
16.3	57.5	1.43
13.3	59.9	1.37
11.4	61.8	1.33
9.68	63.5	1.30
8.70	65.0	1.27
7.62	66.5	1.23
6.86	67.1	1.22
5.89	68.0	1.20
5.12	69.5	1.19
4.43	70.2	1.16
3.85	72.0	1.14
3.37	73.5	1.11
2.98	76.7	1.06
2.65	78.4	1.04
2.37	81.0	1.01
2.15	82.9	0.99
2.0	83.0	0.99

2 liters. As may be seen from the table, the value of i for tetramethylammonium iodide in the neighborhood of 0.01 N is approximately 1.50, while that for sodium acetate is even higher than that of tetramethylammonium iodide, being 1.75 at $V = 41.8$.

Phenol has a dielectric constant of 9.68 and the high values obtained for i are unexpected. The conductance of solutions of tetramethylammonium iodide in phenol at 45° has been measured by Kurtz.[14a] The constants for these solutions are $m = 1.28$, $D = 0.69$, $K = 2.3 \times 10^{-4}$ and $\Lambda_0 = 16.67$. Solutions of tetramethylammonium iodide in phenol thus exhibit an ionization not very different from that found for solutions of typical salts in other solvents, having a dielectric constant in the neighborhood of 10. While the ionization is marked at the lower concentrations, the value is much lower than corresponds to the value of i found by Hartung. Thus, at a concentration 0.01 N, the ionization from the conductance values is 0.194 in contrast to 0.48 from freezing point determinations.

It is evident that there is a wide discrepancy between the values of the ionization as determined by the two methods. It is particularly striking that the values of i found for salts of weak organic acids are higher than those for typical electrolytes. Since phenol is an acid solvent, it is probable that a solvolytic reaction takes place when a salt is dissolved in phenol according to the equation:

$$PhOH + MX = MOPh + HX.$$

If this were the case, we should expect the greatest values of i in the case of salts of weak acids and bases, which would account for the high values found for solutions of tetramethylammonium iodide and sodium acetate. Lacking further experimental material, however, the question must be left open.

The results obtained from molecular weight determinations indicate that, in solvents of intermediate dielectric constant, the values of γ_i approach those of γ_c at low concentrations. At high concentrations the divergence is often great and the variation of the i values depends greatly on the nature of the electrolyte. In solvents of dielectric constant lower than 20, the values of γ by the two methods are not in agreement. This is not surprising, since these solutions may be expected to show large divergences from the laws of ideal systems. So far as may be judged from the available material, however, at very low concentrations, γ_i and γ_c approach a common limit in non-aqueous solutions. The corre-

[14a] Kurtz, Thesis, Clark Univ. (1920).

spondence found between the values of γ_i and γ_c in aqueous solutions appears, therefore, to be a property of electrolytic solutions in other solvents also.

3. *Solubility of Non-Electrolytes in the Presence of Electrolytes.* The solubility of non-electrolytes in water is, in the majority of cases, depressed by the addition of an electrolyte. The effect of the added electrolyte on the solubility depends upon the nature of the substance in question, as well as upon that of the added electrolyte. If reaction takes place between the two, the solubility is naturally influenced by this reaction.

For certain substances, the solubility is very nearly a linear function of the concentration of the added salt, in which case it may be expressed by the equation:

$$S = S_0 + BS_0C \tag{62}$$

where S_0 is the solubility of the non-electrolyte in pure water, S is the solubility in the presence of the salt at the concentration C, and B is the solubility coefficient, which is a constant if the solubility varies as a linear function of the concentration. In general, however, the solubility function is not a linear one. The change in the solubility for a given addition of electrolyte is, as a rule, the greater the smaller the amount of electrolyte added. The solubility is more accurately expressed by the equation:

$$\log \frac{S}{S_0} = \beta C, \tag{63}$$

[15] where β is a constant.

In the following table are given values for the solubility of hydrogen in aqueous solutions of different electrolytes.[16] In pure water, the solu-

TABLE XCIII.

SOLUBILITY OF HYDROGEN IN AQUEOUS SOLUTIONS OF ELECTROLYTES AT DIFFERENT CONCENTRATIONS AT 25°.

$C =$	0.5	1	2	3	4
CH_3COOH	0.0192	0.0191	0.0188	0.0186	0.0186
$CH_2ClCOOH$	0.0189	0.0186	0.0180	....	....
HNO_3	0.0188	0.0183	0.0174	0.0167	0.0160
HCl	0.0186	0.0179	0.0168	0.0159	....
$\frac{H_2SO_4}{2}$	0.0185	0.0177	0.0163	0.0150	0.0141
KOH	0.0167	0.0142	....	....	....
$NaOH$	0.0165	0.0139	0.0097	0.0072	0.0055

[15] Rothmund, *Ztschr. f. Electroch.* 7, 675 (1901); *Ztschr. f. phys. Chem.* *69*, 524 (1909); Nernst, *ibid.*, *38*, 494 (1901).
[16] Geffcken, *Ztschr. f. phys. Chem.* *49*, 257 (1904).

bility of hydrogen at 25° is 0.01926. The results are shown graphically in Figure 48. An examination of the table shows that solubility depression is a specific property of the electrolyte. The depression due to chloroacetic acid is slightly greater than that due to acetic acid. Nitric, hydrochloric and sulphuric acids cause a small, but markedly greater, depression of the solubility. On the other hand, sodium and potassium hydroxides cause a marked depression of the solubility.

The solubilities may be compared by means of the solubility coeffi-

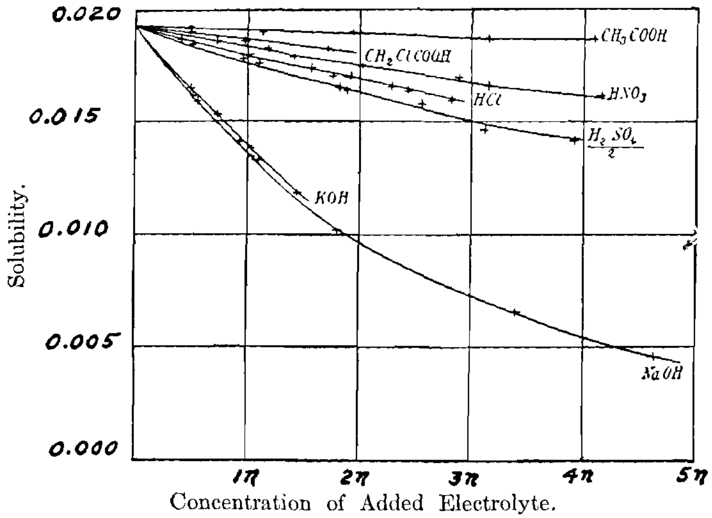

FIG. 48. Solubility of Hydrogen in Water at 25° in the Presence of Electrolytes at Varying Concentrations.

cient for the percentage equivalent solubility change, as defined by the equation:

$$B' = 100 \frac{S_0 - S}{S_0} \times \frac{1}{C}. \tag{64}$$

In Table XCIV are given the values of the percentage equivalent solubility depression of hydrogen, corresponding to Table XCIII. If *the solubility varied as a linear function of the concentration of the salt,* the equivalent percentage solubility depression would be a constant. As may be seen by reference to Figure 48, the curves are convex towards the axis of concentrations, which corresponds to a decrease in the solubility coefficient. In Table XCV are given values of the relative percentage solubility depression for nitrous oxide and in Table XCVI those for oxygen at 25° and 15°. It will be observed, in the first place, that the percentage solubility effect is in certain cases a function of the tempera-

TABLE XCIV.

EQUIVALENT PERCENTAGE SOLUBILITY DEPRESSION FOR HYDROGEN IN WATER AT 25°.

$C =$	0.5	1	2	3	4
CH_3COOH	..	1.0	1.0	1.0	1.0
$CH_2ClCOOH$	3.7%	3.4	3.3	..	..
HNO_3	4.8	4.9	4.8	4.4	4.2
HCl	7.3	7.0	6.4	5.8	..
$\frac{H_2SO_4}{2}$	8.0	8.1	7.7	6.7	..
KOH	26.6	26.4	..	..	..
NaOH	28.6	27.9	24.8	20.9	17.9

TABLE XCV.

RELATIVE PERCENTAGE SOLUBILITY DEPRESSION OF NITROUS OXIDE AT 25° AND 15.°

$C =$	t = 25°					t = 15°				
	0.5	1	2	3	4	0.5	1	2	3	4
HNO_3	−1	−1	−1.1	..	..	0	0	0	..	..
HCl	+5.7	+4.4	+3.1	..	..	+5.9	+5.1	+4.0	..	..
$\frac{H_2SO_4}{2}$	9.4	8.7	7.2	6.3	5.5	11.3	10.2	8.6	7.5	6.9
NH_4Cl	12.4	10.9	..	..	..	12.8	11.2	..	..	..
CsCl	16.8	..	..	..	..	17.5	..	..	..	..
KJ	17.8	17.2	..	..	..	19.5	18.6	..	..	..
KBr	19.5	18.3	..	..	..	20.8	19.4	..	..	..
LiCl	19.8	18.7	..	..	..	20.8	19.9	..	..	..
RbCl	20.5	18.7	..	..	..	21.3	19.7	..	..	..
KCl	20.6	20.0	..	..	..	23.6	20.6	..	..	..
KOH	26.9	26.6	..	..	..	28.3	28.1	..	..	..

TABLE XCVI.

RELATIVE EQUIVALENT PERCENTAGE SOLUBILITY DEPRESSION OF OXYGEN AT 25° AND 15°.

$C =$	t = 25°						t = 15°					
	0.5	1	2	3	4	5	0.5	1	2	3	4	5
HNO_3	4	4	4	..	..	..	8.3	7.4	6.6	..	..	..
HCl	7.8	6.8	6.3	..	..	..	10.4	8.9	8.8	..	..	..
$\frac{H_2SO_4}{2}$	13.0	10.7	9.4	8.4	8.1	7.5	13.8	12.1	10.7	9.9	8.8	8.3
NaCl	30.0	27.6	24.3	..	..	..	30.3	28.4	25.1	..	..	..
$\frac{K_2SO_4}{2}$	35.7	32.8	..	..	..	..	38.0	34.7	..	..	..	..
KOH	36.4	33.1	..	..	..	..	39.7	35.5	..	..	..	..
NaOH	37.7	33.8	28.6	..	..	..	41.3	36.4	30.6	..	..	..

ture, while in other cases the solubility effect is relatively independent of temperature. In the presence of nitric acid, the coefficient for oxygen increases from 4 to 8 per cent, as the temperature falls from 25° to 15°. In the presence of hydrochloric acid the coefficient increases slightly, while in the presence of sulphuric acid the coefficient changes but little. In the presence of sodium chloride, the coefficient is practically identical at the two temperatures. The solubility of nitrous oxide appears to vary less than that of oxygen as the temperature changes.

The order of the electrolytes in terms of their solubility effect is practically the same for different gases. Indeed, in many cases, the solubility coefficients for different gases are very nearly the same for the same electrolyte. An inspection of the tables will show that, in general, the order in which the electrolytes appear is the same. In certain cases, however, the solubility effects show an influence due to the nature of the dissolved gas. For example, in a 1.0 normal solution, the solubility coefficient for hydrogen in the presence of nitric acid is 4.9, that of oxygen is 4, and that of nitrous oxide is — 1 per cent. The negative sign indicates that the solubility is increased on addition of the electrolyte. The solubility effect is smallest in the case of the acids and is greatest in that of the bases. The solubility coefficients for the salts are, in general, slightly smaller than those for the bases.

In Table [17] XCVII are given values of the percentage equivalent solubility depression for a variety of substances in the presence of different electrolytes. A comparison of the results collected in this table shows that the order of electrolytes as regards their effect on the solubility of different substances is practically identical throughout. This is particularly true in the case of those substances where reaction with the electrolyte is not to be expected. The smallest effect for typical salts is observed in the case of ammonium nitrate. However, any general relation between the nature of the electrolyte and the nature of the solubility effect cannot be established. The action is specific in character.

With a few exceptions, the addition of an electrolyte to a solution of a non-electrolyte in water causes a depression in the solubility of the non-electrolyte. This effect, which has been called a "salting out" effect, is not, however, characteristic of electrolytes alone. For example, the percentage equivalent solubility depression of hydrogen in water in the presence of sugar at normal concentration is 32. Similarly, the equivalent depression of hydrogen at the same concentration at 20° is 9.2 for chloral hydrate. The depression for sugar is greater than that for most salts, while that for chloral hydrate is greater than that for the

[17] Euler, *Ztschr. f. phys. Chem.* *49*, 310 (1904).

TABLE XCVII.

EQUIVALENT PERCENTAGE SOLUBILITY COEFFICIENTS FOR VARIOUS SUBSTANCES IN THE PRESENCE OF DIFFERENT ELECTROLYTES.

Salt	H_2	N_2O	N_2	CO_2	H_2S	Ethyl Acetate	Ethyl Ether	Phenyl-thio-urea	SO_2 25°	NH_3 25°	Aniline	Bromine	Iodine
NH_4NO_3	..	..	..	3	1	..	..	—7	—7	..	..	..	..
KJ	..	..	..	..	2	..	26	..	..	6	..	..	..
KBr	..	..	..	..	5.5	..	..	..	..	10	..	..	..
KNO_3	..	..	..	9	9	12	31	8	—6	14	..	15	5
$NaNO_3$	..	..	..	10	11	..	..	10	..	..	..	18	11
LiCl	16	21.4	..	17	..	..	34	..	..	..	23	..	..
KCl	20	22.3	..	..	14.7	30	40	24	—10	13	26	..	..
1/2 $BaCl_2$	..	..	32	..	..	..	..	25	..	..	..	..	..
1/2 $CaCl_2$	21	23.5	..	..	..	..	..	..	..	..	17	..	..
NaCl	21.5	23.9	34	21	15.3	34	42	28	..	11	29	..	..
1/2 $(NH_4)_2SO_4$	..	..	..	..	18	..	..	28	—3	17	..	..	12
1/2 $MgSO_4$	23	29.3	..	30	..	39	..	32	..	23	..	..	..
1/2 $ZnSO_4$	23	..	..	30	..	..	..	..	..	..	..	..	..
1/2 K_2SO_4	..	..	..	..	22	..	..	37	..	..	..	27	15
1/2 Na_2SO_4	27	29.8	..	32	27	43.5	53	41	5	..	..	29	25
1/2 Na_2CO_3	29	..	..	..	..	..	54	38	..	..	..	..	..
NaOH	..	..	..	..	..	..	54	..	..	..	47	..	..
Author	Steiner	Gordon	Braun	Setschenow	McLauchlan	Euler	Euler	Rothm. Biltz	..	..	..	..	..

acids. Obviously, the "salting out" effect cannot well be ascribed to some property peculiar to electrolytes alone.

In a few instances, the addition of a salt causes a marked increase in the solubility of a non-electrolyte. This is the case with ether in water in the presence of sodium salts of aromatic acids.[18] While the salts of the aliphatic acids cause a marked depression in the solubility, those of the aromatic acids cause an increase in solubility.

In Table XCVIII are given values of the equivalent percentage solubility increase of ether in water due to the addition of 0.5 N salts of different acids.

TABLE XCVIII.

SOLUBILITY CONSTANTS FOR ETHER IN THE PRESENCE OF SODIUM SALTS OF AROMATIC ACIDS.

Salt	Solubility	Solubility Coefficient
0.5 N Sodium Phthalate	5.88	1.5
0.5 N Sodium Cinnamate	6.29	15.0
0.5 N Sodium Benzoate	5.99	4.8
0.5 N Sodium Salicylate	6.44	20.0
0.5 N Sodium Benzenesulphonate	6.05	7.0

The solubility of ether is given in the second column. The solubility of ether in pure water is 5.85 grams per 100 grams of water at 28°. It is evident that the so-called "salting out" effect is not a property characteristic of all electrolytes.

It is of interest to examine the solubility effects in non-aqueous solutions. Here the data are very meager. Thorin[19] has measured the solubility of phenylthiourea in ethyl alcohol at 28°. The results are

TABLE XCIX.

SOLUBILITY OF PHENYLTHIOUREA IN ETHYL ALCOHOL IN THE PRESENCE OF ELECTROLYTES.

Electrolyte	Concentration	Solubility	B'
LiCl	0.168 norm.	0.2274 norm.	60
"	0.337	0.2360	42
"	0.673	0.2440	27
"	1.346	0.2494	15

[18] *Thorin, Ztschr. f. phys. Chem.* 89, 688 (1915).
[19] *Ibid.*, 89, 691 (1915).

TABLE XCIX.—*Continued*

Electrolyte	Concentration	Solubility	B′
$CaCl_2$	0.061	0.2101	28
"	0.122	0.2135	28
"	0.244	0.2194	25
"	0.487	0.2279	21
"	0.975	0.2372	15
NaJ	0.043	0.2102	42
"	0.086	0.2148	46
"	0.172	0.2198	37
"	0.343	0.2271	29
"	0.685	0.2359	21
NaBr	0.022	0.2098	73
"	0.043	0.2194	66
"	0.086	0.2165	57
"	0.172	0.2257	54

given in Table XCIX. The solubility in pure alcohol is 0.2065 grams per hundred grams of solvent. The equivalent percentage solubility increase is given in the last column under *B′*.

It will be observed that the solubility coefficient is initially quite large and decreases markedly at the higher concentrations. The solubility is in all cases increased, but, as in the case of aqueous solution, the solubility effect is a property of the electrolyte in question. The effect is greatest for lithium chloride, in which case the solubility is increased approximately 20 per cent in a normal solution of the electrolyte.

Some writers have ascribed the depression of the solubility of non-electrolytes in water, due to electrolytes, to the action of the ions upon the non-electrolyte. If any interaction of this kind actually takes place, it must be of a secondary nature, and greatly qualified by the nature of the ions with which the charges are associated. The increase in the solubility of phenylthiourea in alcohol clearly indicates that the action of the salt upon the non-electrolyte is greatly affected by the nature of the solvent medium. Further experimental data on the effects of salts on the solubility of non-electrolytes in non-aqueous solutions are of much interest.

4. *Solubility of Salts in the Presence of Non-Electrolytes.* The solubility of salts in aqueous solutions is in general depressed by the addition of non-electrolytes. The solubility change, as a rule, follows very nearly, although not quite, a linear relation. In the following table are given values for the solubility of lithium carbonate in water at 25° in

the presence of various non-electrolytes, at different concentrations.[20] The solubility of lithium carbonate in pure water is 0.1687 equivalents per liter.

TABLE C.

SOLUBILITY OF LITHIUM CARBONATE IN THE PRESENCE OF NON-ELECTROLYTES.

Mols of non-electrolyte	⅛-	¼-	½-	1-norm.
1. Methyl alcohol	....	0.1604	0.1529	0.1394
2. Ethyl alcohol	0.1614	0.1555	0.1417	0.1203
3. Propyl alcohol	0.1604	0.1524	0.1380	0.1097
4. Amyl alcohol (tertiary)	0.1564	0.1442	0.1224	0.0899
5. Acetone	0.1600	0.1515	0.1366	0.1104
6. Ether	0.1580	0.1476	0.1300	....
7. Formaldehyde	0.1668	0.1653	0.1606	0.1531
8. Glycol	0.1660	0.1629	0.1565	0.1472
9. Glycerine	0.1670	0.1647	0.1613	0.1532
10. Mannite	0.1705	0.1737	0.1778	....
11. Grape sugar	0.1702	0.1728	0.1752	0.1778
12. Cane sugar	0.1693	0.1689	0.1661	0.1557
13. Urea	0.1686	0.1673	0.1643	0.1605
14. Thiourea	0.1667	0.1643	0.1600	0.1523
15. Dimethylpyrone	0.1562	0.1460	0.1284	0.0992
16. Ammonia	0.1653	0.1630	0.1577	0.1466
17. Diethylamine	0.1589	0.1481	0.1283	0.0937
18. Pyridine	0.1592	0.1503	0.1347	0.1091
19. Piperidine	0.1584	0.1488	0.1320	0.1009
20. Urethane	0.1604	0.1525	0.1377	0.1113
21. Acetamide	....	0.1614	0.1520	0.1358
22. Acetonitrile	0.1618	0.1556	0.1429	0.1178
23. Mercuric cyanide	0.1697	0.1704	....	....

It will be observed that, with a few exceptions, of which mannite and grape sugar are the most striking examples, the solubility is depressed by the addition of non-electrolytes. In general, the depression is the greater the smaller the dielectric constant of the added non-electrolyte, although this relation does not hold exactly, since, for example, the addition of ether causes a smaller decrease in the solubility than does that of amyl alcohol. With increasing complexity of the carbon group the depression of the solubility, in general, increases. The solubilities may be expressed approximately as a function of concentration by Equation 63.

In the following table are given the values of 100 β for solutions of a number of salts in water in the presence of non-electrolytes.[21] The non-

[20] Rothmund, *Ztschr. f. phys. Chem.* 69, 531 (1909).
[21] Rothmund, *loc. cit.*

TABLE CI.

SOLUBILITY OF $LiCO_3$, Ag_2SO_4, $KBrO_3$, $KClO_4$, $Sr(OH)_2.8H_2O$ AT 25° IN THE PRESENCE OF ELECTROLYTES.

Values of 100 β.

	Li_2CO_3	Ag_2SO_4	$KBrO_3$	$KClO_4$	$Sr(OH)_2.8H_2O$
Amyl alcohol (tert.)..	63.0	54.2	44.3	28.5	54.1
Dimethylpyrone	56.1	..	43.8	19.3	71.0
Ether	52.4	52.2	38.1	19.8	51.3
Dimethylpyrone.......	54.6	42.7	..	..	..
Piperidine	50.5	..	37.6	..	..
Formaldehyde	(9.5)	32.4	37.1	..	..
Methylal	..	53.1	33.1	10.5	..
Propyl alcohol	41.7	40.4	31.2	18.7	32.6
Pyridine	44.4	..	28.3	9.0	36.7
Methylacetate	..	46.5	25.9	6.4	..
Acetonitrile	34.6	(—134.8)	..	..	..
Ethyl alcohol	33.6	31.9	24.9	10.8	22.8
Chloral	..	27.9	..	..	..
Acetone	42.4	39.1	23.5	3.3	37.5
Phenol	..	(—70.0)	23.0	16.0	..
Cane sugar	(5.0)	(—1.5)	20.7	..	..
Urethane	41.0	36.7	18.7	10.5	..
Methyl alcohol	19.3	22.1	14.7	10.1	3.4
Acetamide	20.8	10.7	14.4	3.8	..
Ammonia	14.0	..	14.3	0.1	12.3
Glycol	14.2	10.3	10.3	8.2	(—19.9)
Thiourea	10.3	..	..	..	..
Glycerine	9.3	3.4	11.6	9.8	(—54.3)
Mannite	(—10.5)	(—20.3)	11.6	..	(—174)
Acetic acid	..	12.3	9.4	1.5	..
Grape sugar	(—6.6)	(—11.6)	6.3	..	..
Formamide	..	(—2.2)	1.1	—8.5	..
Urea	4.5	(—25.3)	0.0	—4.7	3.6
Glycocoll	..	(—96.3)	—9.4	..	..

electrolytes are arranged vertically in the order of their effect on the solubility of potassium bromate. Those values which appear in parentheses in the table are such in which interaction between the non-electrolyte and the electrolyte probably occurs. A negative value of the solubility coefficient indicates an increase in the solubility. With the possible exception of potassium bromate in the presence of glycocoll and potassium perchlorate in the presence of formamide and urea, the increased solubilities are probably to be ascribed to interaction between the electrolyte and the non-electrolyte.

For lithium carbonate, silver sulphate, potassium bromate, and potassium perchlorate, there is a rough parallelism in the order of the solubility effects among the different electrolytes in the presence of a non-electrolyte, although numerous exceptions occur, particularly in the case of lithium carbonate. So, also, the solubility effect in general decreases in the order lithium carbonate, silver sulphate, potassium bromate, potassium perchlorate, although here, again, exceptions are found. There can be no question, however, that a parallelism exists between the solubility effects for different salts and for different electrolytes. Roughly, those non-electrolytes which suffer the greatest solubility change on the addition of a non-electrolyte cause the greatest change in the solubility of a given electrolyte, and those electrolytes which cause the greatest change in the solubility of a given non-electrolyte suffer the greatest solubility change on the addition of a given non-electrolyte. These relations, however, are only roughly true. It is again evident that the effect of different non-electrolytes on the solubility of electrolytes is primarily a function of the nature of the electrolyte and of the added non-electrolyte. Similar measurements on the solubility effects in non-aqueous solvents do not exist.

5. *Solubility of Electrolytes in the Presence of Other Electrolytes.* If an electrolyte is added to a solution of another electrolyte, which is present as a solid phase in equilibrium with its solution, the solubility effect will obviously depend upon the interaction between the two electrolytes. Since electrolytes in solution are ionized and equilibrium establishes itself almost instantaneously, it is to be expected that various effects will be observed. We have to consider here two cases which are of practical importance: First, the solubility of an electrolyte in the presence of another electrolyte with a common ion; and, second, the solubility of an electrolyte in the presence of another electrolyte without a common ion.

a. *Solubility of Weak Electrolytes in the Presence of Strong Electrolytes with an Ion in Common.* If the law of mass-action is applicable, the addition of a binary electrolyte to a second binary electrolyte having an ion in common should cause a depression in the solubility of the second electrolyte. We have the equations:

$$\frac{M_1^+ \times X_1^-}{S_u} = K_1$$

$$\frac{M_2^+ \times X_1^-}{M_2X_1} = K_2,$$

it being assumed that the two electrolytes have a negatives ion X^- in common. Here, S_u is the concentration of the un-ionized fraction of the *first* electrolyte, which is assumed to be present in excess, so that there exists an equilibrium between the solid salt M_1X_1 and the solution. If the laws of ideal solutions hold, the concentration S_u of the un-ionized fraction of the first, salt should remain constant. The total concentration S of the first salt is then given by the equation:

$$S = M^+ + S_u. \tag{65}$$

If a second electrolyte with a common ion X_1 is added, then, in the mixture, we have the equilibrium expressed by the equation:

$$\frac{M_1^+(M_1^+ + M_2^+)}{S_u} = K_1, \tag{66}$$

where $M_1^+ + M_2^+$ is the concentration of the common ion X^-, which we may write ΣC_i. It follows from Equation 66 that:

$$M^+ = \frac{K_1 S_u}{\Sigma C_i} \tag{67}$$

and substituting for this value in Equation 65, we have for the solubility the expression:

$$S = S_u + \frac{K_1 S_u}{\Sigma C_i}, \tag{68}$$

An examination of this equation shows that the addition of an electrolyte with a common ion reduces the solubility of the first electrolyte. If we plot values of S as ordinates and those of ΣC_i as abscissas, the resulting curve will be a rectangular hyperbola, whose axis is raised above the origin by the distance S_u. As the concentration of the added electrolyte, and consequently the concentration of the common ion, is increased indefinitely, the solubility approaches the value S_u as a limit. The representation of solubility results is greatly simplified if the solubility is plotted against the reciprocal of the common ion concentration, in which case a linear curve obviously results. This curve ends in a point

$$S_0 = S_u + M_{01}^+$$

where S_0 is the solubility of the first electrolyte in pure water and M_{01}^+ is the ion concentration in this solution. As the reciprocal of the total ion concentration, $1/\Sigma C_i$, or the common ion dilution ΣV_i, decreases, the solubility decreases as a linear function of this variable, approaching the value $S = S_u$ at $1/\Sigma C_i = 0$.

If S_u is a constant, as it is if the laws of ideal solutions hold, and if K_1 is a constant, then it follows from Equation 66 that

$$M_1^+ \times X^- = K_1 S_u = K, \qquad (69)$$

where X^- is the concentration of the common ion in the solution, and K is a constant. For an electrolyte in solution in equilibrium with its solid phase, the product of the concentrations of the ions remains constant, provided that the laws of dilute solutions hold. According to these considerations, the solubility of a given electrolyte may be depressed to a value which corresponds to the concentration of the un-ionized fraction in a solution of the pure electrolyte in equilibrium with its solid phase.

The foregoing relations are based on the assumption that the laws of dilute solutions are applicable. As we have seen, this condition is not fulfilled in solutions of strong electrolytes. The effect of the presence of strong electrolytes upon the solubility of other strong or weak electrolytes can, therefore, be determined by experiment only.[21a] The concentration of the various molecular species in the mixture cannot be determined, even though the solubility of the first electrolyte is known, unless a law is assumed governing the equilibrium of the various electrolytes present in the mixture; and the results obtained for the concentration of the ionized and the un-ionized fraction of the first salt in the mixture, as calculated, will depend upon the laws assumed as governing the equilibrium in the mixture.

We shall first examine the effect of strong and weak electrolytes upon the solubility of weak electrolytes; that is, electrolytes which conform to the simple mass-action law. Such determinations have been made by Kendall.[22]

In Table CII is given values for the solubility of a number of weak acids in the presence of other acids, both weak and strong.

The results are shown graphically in Figures 49 and 50. Considering first the solubility of orthonitrobenzoic acid and salicylic acid in the

[21a] It is evident from Equation 69 that K_1 and S_u might vary in such a manner that their product would remain constant, in which case the ion product would remain constant. It is very improbable, however, that such a compensation actually occurs.

[22] Kendall, *Proc. Roy. Soc.* 85 *A*, 218 (1911).

TABLE CII.

SOLUBILITY OF WEAK ACIDS IN THE PRESENCE OF OTHER ACIDS.

A. *Salicylic Acid in the Presence of Formic Acid.*

Formic acid, per cent.	Solubility, gravimetric, mols per liter.	Solubility, volumetric, mols per liter.
0.00	0.01631	0.01634
0.24	....	0.01531
0.46	....	0.01474
0.625	0.01484	....
1.25	0.01496	....
2.5	0.01536	....
5.0	0.01716	....
10.0	0.02101	....

B. *Solubility of Hippuric Acid in the Presence of Formic Acid.*

Formic acid, per cent.	Solubility, *gravimetric,* mols per liter.	Solubility, *volumetric,* mols per liter.
0.00	0.02045	0.02048
1.25	0.02014	....
2.5	0.02078	....
5.0	0.02275	....
10.0	0.02661	....

C. *Solubility of Salicylic Acid in the Presence of Acetic Acid.*

Acetic acid, per cent.	Solubility, gravimetric, mols per liter.
0.00	0.01631
0.625	0.01691
1.25	0.01745
2.5	0.01846
5.0	0.02059

Solubility of Salicylic Acid in the Presence of Hydrochloric Acid.

Hydrochloric acid, normal.	Solubility, gravimetric, mols per liter.	Solubility, volumetric, mols per liter.
....	0.01631	0.01634
0.0179	....	0.01290
0.0357	....	0.01238
0.125	0.01214	....
0.25	0.01194	....
0.5	0.01123	....

TABLE CII.—*Continued*

E. *Solubility of o-Nitrobenzoic Acid in the Presence of Hydrochloric Acid.*

Hydrchloric acid, normal.	Solubility, gravimetric, mols per liter.	Solubility, volumetric, mols per liter.
....	0.04320	0.04360
0.0179	....	0.03681
0.0357	....	0.03390
0.125	0.02980	....
0.25	0.02922	....
0.5	0.02846	....

presence of hydrochloric acid, it will be observed that the solubility decreases greatly on the initial addition of hydrochloric acid, after which the solubility decreases slightly, practically as a linear function of the concentration. In the presence of the weaker acids, the initial decrease

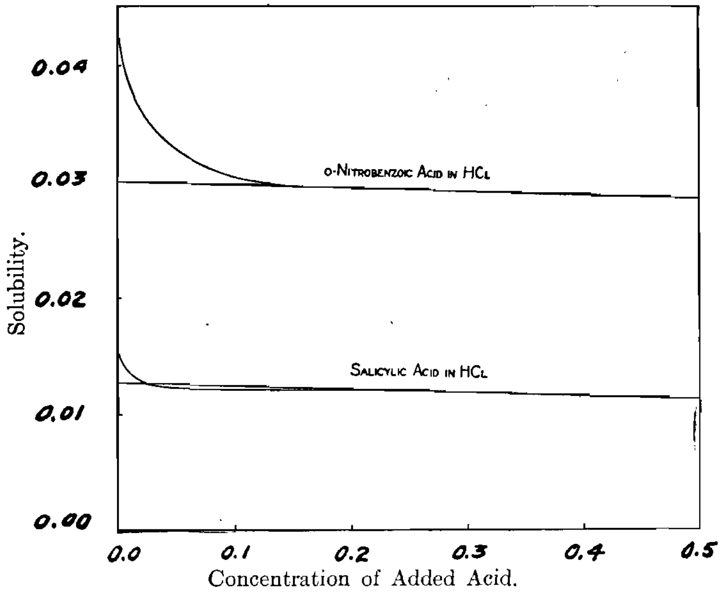

Fig. 49. Solubility of Moderately Strong Organic Acids in Water in the Presence of Hydrochloric Acid at 25°.

is relatively slight, and this decrease is the smaller the weaker the added acid. The solubility of salicylic acid in the presence of acetic acid increases from the beginning. In the case of the organic acids the solubility eventually increases, practically as a linear function of the concentration of the added acid. The results are in harmony with the

assumption that the initial depression in the solubility of the acid is due to the depression of its ionization. Acetic acid is so weak that, even at fairly high concentrations, it has no appreciable effect on the ionization of salicylic acid, and consequently the resulting curve merely measures the increase in the solubility of the un-ionized fraction. In the case of hippuric and salicylic acids in formic acid, the added acid is sufficiently strong to practically completely repress the ionization of salicylic acid present in solution. In these cases, therefore, there is an initial decrease in the solubility, while finally, when the ionization is completely repressed, the solubility is increased, owing, presumably, to the increased solubility of the un-ionized molecules of the first acid on addition of the second. By extrapolating the linear solubility curves backwards, until they inter-

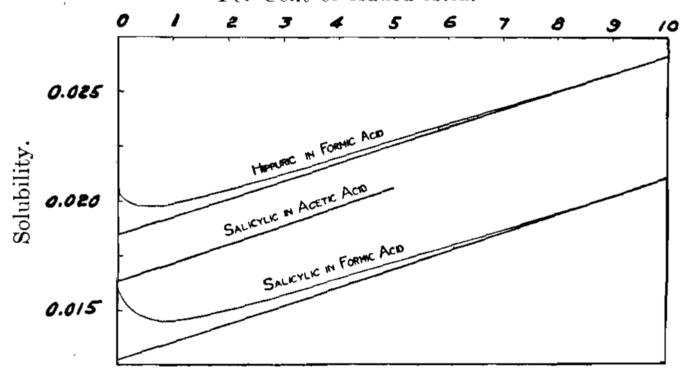

Fig. 50. Solubility of Weak Organic Acids in Water in the Presence of Other Organic Acids at 25°.

sect the axis of solubility, the intercepts on this axis correspond approximately to the solubility of the un-ionized fraction in pure water.

It will be noted that the solubility of salicylic acid and of orthonitrobenzoic acid is depressed according to the requirements of the mass-action law not only on addition of weak acids, but also on addition of hydrochloric acid. In this case, the solubility of the un-ionized fraction in the more concentrated solutions decreases slightly with increasing concentration of hydrochloric acid. The initial depression effect is marked, particularly in the case of orthonitrobenzoic acid, which is a fairly soluble acid. Apparently, the addition of a strong acid to a solution of a weak acid, as well as the addition of a weak acid to a solution of a weak acid, does not greatly alter the ionization constant of weak acids. The ionization constant of salicylic acid at 25° is 1.02×10^{-3}; that of hippuric acid is 2.22×10^{-4}; and orthonitrobenzoic acid 6.16×10^{-3}.

Kendall and Andrews[22a] have recently extended the investigation of the solubility of acids in the presence of weak acids. They have measured the solubility of acids of varying strength and solubility in the presence of both strong and weak acids up to high concentrations. They include hydrogen sulphide, carbonic acid, boric, oxalic, succinic, trichloroacetic, *m*-nitrobenzoic, 3-5-dinitrobenzoic, benzoic, picric and β-naphthalene sulphonic acids in the presence of hydrochloric acid; and suberic, mandelic, succinic, oxalic, tartaric and boric acids in the presence of acetic acids up to concentrations of 10 normal added acid. They have also measured the solubility of boric, benzoic and salicylic acids in the presence of nitric acid.

The solubility of all acids on addition of a strong acid is initially decreased. On addition of larger amounts of the strong acid the solubility, with a few exceptions, passes through a minimum. At high concentrations of the added acid, the solubility increase is very marked in some cases while, in a few, the minimum is lacking. The initial decrease appears to be due to a repression of the ionization of the saturating acid. The stronger the acid, the greater is the initial depression, while in the case of very weak acids the initial depression is wanting. The minimum solubility of an acid is much lower than corresponds to the concentration of its un-ionized molecules in pure water. This is ascribed to the depression of the solubility because of hydration effects accompanying the addition of the strong acid. It may be noted that the maximum depression of hydrogen sulphide and carbonic acids is very low, amounting to only a few per cent. The final rise in the solubility curve is ascribed to the formation of compounds between the two acids at high concentrations. This view is supported by the results of conductance measurements which indicate the formation of complexes. This accounts for the widely divergent effect of strong acids on different weak acids at higher concentrations. The solubility curves for weak acids in the presence of acetic acid exhibit a great variety of form. Here, the common ion effects at low concentration of added acid are approximately as might be expected.

The effect of strong and weak acids on the un-ionized fraction of weak acids does not differ greatly from that observed in the case of non-electrolytes. For example, the solubility of hydrogen in water is only very slightly depressed due to the addition of acetic acid, but somewhat more strongly due to the addition of hydrochloric acid. In a normal solution of hydrochloric acid, the solubility depression in the case of hydrogen is 7 per cent and that in the case of the undissociated fraction of orthonitrobenzoic acid 10 per cent. The percentage depression in the case of sali-

[22a] Kendall and Andrews, *J. Am. Chem. Soc.* *43*, 1545 (1921).

cylic acid is considerably greater. It appears, therefore, that, on the addition of an electrolyte, so far as the solubility relations are concerned, substances with polar molecules are affected in the same way as are those with non-polar molecules. With polar substances, the same specific effects are found which are characteristic of non-polar substances. At high concentrations of the added acid, the specific nature of the effects indicates some manner of interaction between the two acids.

b. *The Solubility of Strong Binary Electrolytes in the Presence of Other Strong Electrolytes.* The solubility of a strong electrolyte is, in general, depressed on the addition of another strong electrolyte having a common ion. On the addition of a salt without a common ion, the solubility is in general increased, presumably owing to the formation of un-ionized molecules as a consequence of a metathetic reaction. The relations are much simpler with binary electrolytes than with electrolytes of higher type. The solubility relations are also greatly affected by the concentration of the electrolyte, whose solubility is under consideration.

In Table CIII are given values for the solubility of thallous chloride in water at 25° in the presence of various electrolytes.[23] The results are

TABLE CIII.

SOLUBILITY OF THALLOUS CHLORIDE IN THE PRESENCE OF OTHER ELECTROLYTES.

Conc. of added salt	HCl	KCl	$BaCl_2$	$TlNO_3$	Tl_2SO_4	KNO_3	K_2SO_4
10	16.07	16.07	16.07	16.07	16.07	16.07	16.07
20	..	..	..	..	10.34	17.16	17.79
25	8.66	8.69	8.98	8.80	..	..	..
50	5.83	5.90	6.18	6.24	6.77	18.26	19.42
100	3.83	3.96	4.16	4.22	4.68	19.61	21.37
200	2.53	2.68	2.82	..	..	..	..
300	..	..	..	..	..	23.13	26.00
1000	..	..	..	..	..	30.72	34.16

shown graphically in Figure 51. An examination of the table and the figure shows that the solubility change in the case of different electrolytes is of the same order of magnitude for salts of the same type. The depression due to the addition of hydrochloric acid is slightly greater than that due to potassium chloride or thallous nitrate. Ternary salts, having an ion in common with thallous chloride, cause a depression which is very nearly the same as that of binary salts. The solubility is markedly increased due to the addition of salts without a common ion. While the solubilities due to the addition of different salts differ, this

[23] Bray and Winninghoff, *J. Am. Chem. Soc.* 33, 1671 (1911).

difference is in general much smaller than in the case of solutions of non-electrolytes.

It is not possible to determine the concentration of the un-ionized fraction in mixtures of electrolytes without assuming a law governing

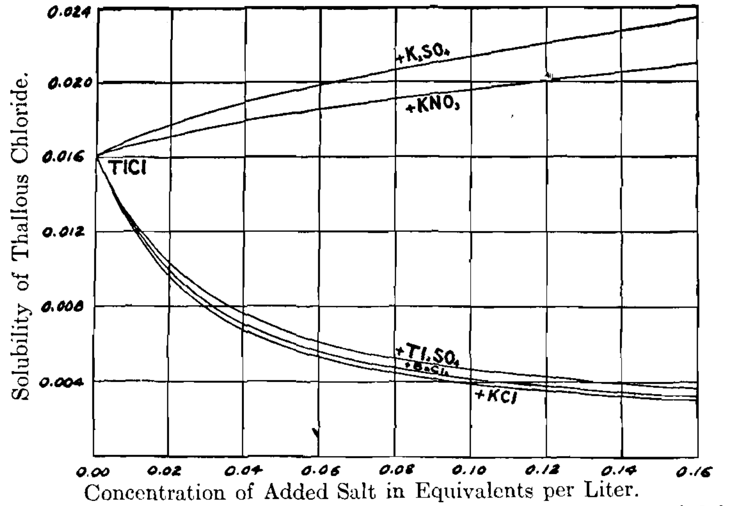

Fig. 51. Solubility of Thallous Chloride in Water in the Presence of Other Electrolytes.

the ionization of electrolytes in mixtures. As a rule, the iso-ionic principle has been employed for this purpose. In Table CIV are given values for the concentration of the un-ionized fraction, TlCl, and the ion product, $Tl^+ \times Cl^-$, for solutions of thallous chloride in the presence of different electrolytes at 25° [24], the isohydric principle being assumed to hold for the mixtures.

TABLE CIV.

Calculated Values of the Ion Product and the Concentration of the Un-ionized Fraction for Thallous Chloride in Water at 25° in the Presence of Different Electrolytes.

Added Salt	Conc.	0	20	25	50	100	300
1/2 K_2SO_4	TlCl	1.755	1.338	..	1.120	0.966	0.768
	$Tl^+ \times Cl^-$	204.9	211.0	..	218.3	229.7	258.6
1/2 Tl_2SO_4	TlCl	1.755	1.465	..	1.239	1.087	..
	$Tl^+ \times Cl^-$	204.9	208.1	..	215.7	231.3	..
KNO_3	TlCl	1.755	1.343	..	1.124	0.968	0.775
	$Tl^+ \times Cl^-$	204.9	217.4	..	229.1	243.0	279.2
	Conc.	0	20	25	50	100	200
KCl	TlCl	1.755	..	1.390	1.204	1.061	0.94
	$Tl^+ \times Cl^-$	204.9	..	218.1	229.6	256.3	290.0

[24] Bray and Winninghoff, *loc. cit.*

It will be observed that, according to these calculations, the concentration of the un-ionized fraction decreases markedly as the concentration of the added electrolyte increases. In a 0.3 normal solution of potassium sulphate, the calculated concentration is less than one half that in pure water. The ion product increases due to the addition of the second electrolyte, this increase depending upon the nature of the added electrolyte. On the addition of 0.3 N equivalents of potassium sulphate, the ion product increases from 204.9 to 258.6. On the addition of 0.2 N equivalents of potassium chloride, the ion product increases from 204.9 to 290.0. The increase in the case of potassium chloride, therefore, is approximately twice that for potassium sulphate. If the assumptions underlying these calculations are correct, the concentration of the un-ionized fraction is greatly reduced on the addition of a relatively small amount of a second electrolyte. Since it has commonly been assumed that the isohydric principle holds for strong electrolytes, many writers have accepted as correct the result that the concentration of the un-ionized fraction of the salt is greatly depressed on the addition of an electrolyte. As was pointed out in a preceding section, the applicability of the iso-ionic principle to mixtures of strong electrolytes is doubtful. It is doubtful, therefore, that the above values represent correctly the state of the solutions in question.

The solubility depression of the un-ionized fraction is much greater than might be expected from the effect of electrolytes upon the solubility of non-electrolytes. The solubility depression of hydrogen in water at 15° for different salts at normal concentration is in the neighborhood of 20 per cent, that of oxygen in the neighborhood of 30 per cent, and that of nitrous oxide in the neighborhood of 20 per cent. The solubility depression of phenylthiourea at normal concentration of the added salt is 24 per cent for potassium chloride, 10 per cent for sodium nitrate, and for ammonium nitrate there is a solubility increase of 7 per cent. The solubility curves, moreover, while not quite linear, are only slightly convex toward the axis of concentrations. Furthermore, on the addition of hydrochloric acid, the solubility depression of non-electrolytes is relatively very small. At normal concentration and 25°, it is 7 per cent for hydrogen, 6.8 per cent for oxygen, and 4.4 per cent for nitrous oxide. From the effect of electrolytes on the solubility of non-electrolytes, it must be concluded, not only that the effect varies greatly with the nature of the added electrolyte, but, also, that the magnitude of the effect is much lower than that derived from the values calculated on the basis of the isohydric principle. Furthermore, it follows from the work of Ken-

dall,[25] discussed in the preceding section, that even polar molecules, such as we have in the weak acids, are affected only to a slight extent by the presence of strong acids. The depression of the concentration of the un-ionized fraction of a strong electrolyte in equilibrium with its solid phase, due to the addition of other electrolytes, has been ascribed to interaction between the ions and the un-ionized fraction of the first salt, and the salting out effect in the case of non-electrolytes has been cited in support of this hypothesis. From the foregoing analysis, however, it would appear that the behavior of non-electrolytes, as well as that of weak electrolytes, in the presence of strong electrolytes, lends little support to this hypothesis. On the whole, it appears much more likely that the concentration of the un-ionized fraction varies as a function of the nature of the added electrolyte, and that, in general, it varies less than indicated by the calculated values given above.

According to the above calculation, the ion product varies considerably with the concentration of the added electrolyte and depends, to a considerable extent, upon the nature of this electrolyte. Observations on the solubility of salts in the presence of other salts indicate that, even in the case of strong electrolytes, the ion product remains approximately constant on the addition of other electrolytes.[26] It is at once evident that if the concentration of the un-ionized fraction is only slightly decreased on the addition of a second electrolyte, the concentration of the ions is appreciably smaller than that derived from calculations on the basis of the iso-ionic principle. The result is to render the value of the ion product approximately constant and independent of the concentration of the added electrolyte.

As we have seen, the conductance of mixtures of hydrochloric acid and sodium chloride, calculated on the assumption that the equilibrium in the mixture is governed by the isohydric principle, is not in accord with the experimentally determined values. On the other hand, we saw that, in the more dilute solutions, the observed values agree very nearly with the values calculated on the assumption that in the mixture the equilibrium conforms to Equation 52. It is evident that if C_u remains constant in the mixture, P_i will likewise remain constant. If, therefore, the concentration of the un-ionized fraction of a salt remains constant, the ion product should also remain constant according to this principle. Assuming this principle to hold, we may calculate values for the concentration of the un-ionized fraction and for the ion product in the case of a salt in equilibrium with its solid phase in the presence of a second

[25] Kendall, *loc. cit.*
[26] Stieglitz, *J. Am. Chem. Soc.* *30*, 946 (1908).

electrolyte. For thallous chloride in the presence of potassium chloride the following results are obtained:

TABLE CV.

VALUE OF THE UN-IONIZED FRACTION AND OF THE ION PRODUCT FOR THALLOUS CHLORIDE IN WATER AT 25°, IN THE PRESENCE OF POTASSIUM CHLORIDE, ASSUMING EQUATION 52.

C of KCl	0	25	50	100	200
S_u	0.001755	0.001746	0.001734	0.001703	0.001586
$P_i \times 10^4$	2.052	2.039	2.011	1.973	1.808

The calculations are based upon Λ_0 values identical with those of Bray and Winninghoff.[27] Taking into account the uncertainties in the values of Λ_0, as well as in the values of the solubilities themselves, it appears from an inspection of the above table that, assuming the equilibrium in the mixture to be governed by Equation 52, the concentration of the un-ionized fraction in the mixture, as well as the value of the ion product, remains substantially constant up to a concentration of approximately 0.1 N potassium chloride. For example, in the presence of 0.1 N potassium chloride, the concentration of the un-ionized fraction as calculated is 0.001703 as against 0.001755 for a solution of thallous chloride in water alone. This represents an increase of only 1.9 per cent. Similarly, the ion product over the same concentration interval varies only 4 per cent. The increase in the value of the ion product and the decrease in the concentration of the un-ionized fraction of a binary salt, on addition of a second electrolyte with a common ion, is therefore primarily a consequence of the form of the function assumed as governing the equilibrium in the mixture. The manner in which P_i and C_u vary on the addition of a second electrolyte remains uncertain so long as the law governing the equilibria in mixtures remains unknown.

If the value of the ion product and the concentration of the un-ionized fraction remain constant, the solubility of the salt is given by the equation:

$$S = S_u + \frac{K_1 S_u}{\Sigma C_i} \qquad (70)$$

where S is the solubility of the salt at any concentration, S_u is the concentration of the un-ionized fraction, which is independent of concentration, ΣC_i is the concentration of the common ion, and K_1 is a constant for the mixture whose value may be determined from the ioniza-

[27] Bray and Winninghoff, *loc. cit.*

tion function of the pure electrolyte. The value of ΣC_i may be calculated by means of Equation 52. From Equation 70, it is evident that the total solubility of the salt S in the presence of another salt with a common ion is a linear function of the reciprocal of the common ion concentration $\frac{1}{\Sigma C_i}$. In Figure 52 are plotted solubility values for TlCl

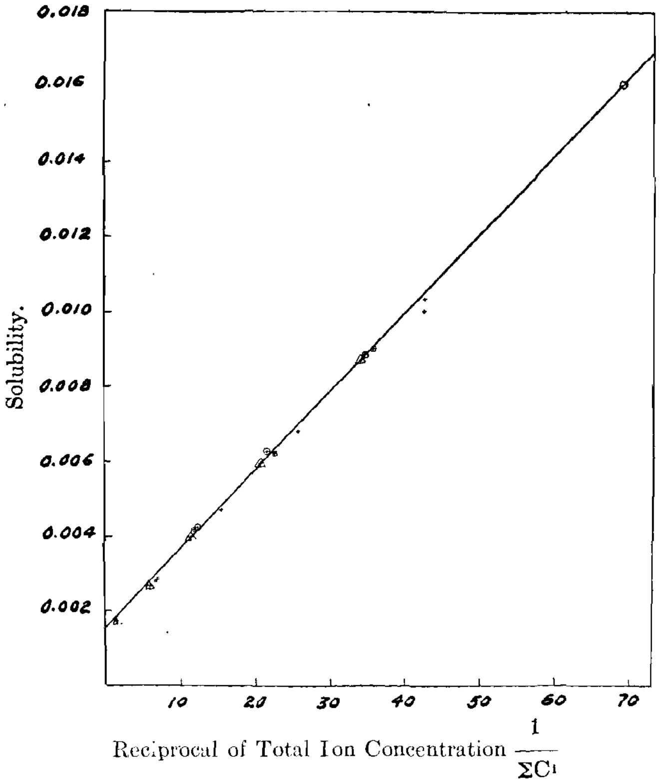

FIG. 52. Representing the Solubility of Thallous Chloride as a Function of the Reciprocal of the Total Ion Concentration.

in the presence of thallous sulphate, thallous nitrate, potassium chloride and barium chloride. In the case of KCl as added salt, the values of ΣC_i have been calculated according to Equation 52. The other values of ΣC_i are those of Bray,[28] which are based on the isohydric principle. Since the difference in the values of ΣC_i as derived by Equations 51 and 52 is not great, an approximate comparison is afforded by the values

[28] Bray, *J. Am. Chem. Soc.* 33, 1674 (1911).

employed. On examination of the figure, it will be seen that, up to a concentration of 0.1 N of added salt, the points lie very nearly upon a straight line, and, furthermore, that the solubility values due to the addition of different electrolytes conform very nearly to the same straight line. It cannot be said that Equation 70 actually holds for the mixture; nevertheless, the effect of different electrolytes upon the solubility of thallous chloride is much more uniform in character when treated in this way than when treated according to the isohydric principle. Up to 0.1 N concentration of added salt, the solubilities differ only a few per cent from the linear relation.

The conclusion to be drawn, however, is not so much that the ion product and the concentration of the un-ionized fraction as calculated according to Equation 52 remain constant for a salt in equilibrium with its solution as that the values obtained for the concentrations of the various molecular species present in the mixture depend upon the law assumed to govern the equilibrium in the mixture. The conclusion reached by many writers, that the concentration of the un-ionized fraction decreases greatly with increasing concentration of the added electrolyte,[29] is a consequence of the assumption of the isohydric principle as a basis for calculating the concentrations of the various molecular species present. As was shown by Bray and Hunt,[30] the specific conductances of mixtures of sodium chloride and hydrochloric acid, calculated on the basis of the isohydric principle, are throughout greater than the measured ones. It follows, therefore, that the concentrations of the ions as calculated according to this assumption are greater than the true ones. Consequently, the concentration of the un-ionized fraction, which is obtained by difference, is obviously found too low. It is not probable that the concentration of the un-ionized fraction of an electrolyte in equilibrium with its solutions will be entirely unaffected by the addition of other electrolytes, since, as we have seen in a preceding section, the solubility of non-electrolytes is influenced by the addition of electrolytes. We might expect, however, that the change in the concentration of the un-ionized fraction would not differ greatly from that of non-electrolytes under similar conditions. This conclusion is further borne out by the results of Kendall[31] on the solubility of organic acids in the presence of other acids.

In the case of salts which are more soluble, the effect of a second electrolyte upon the solubility is, in general, much smaller and, in some

[29] Noyes, *J. Am. Chem. Soc.* *33*, 1643 (1911); *Stieglitz, ibid.*, *30*, 946 (1908); Arrhenius, *Ztschr. f. phys. Chem.* *31*, 224 (1899).
[30] Bray and Hunt, *J. Am. Chem. Soc.* *33*, 781 (1911).
[31] Kendall, *loc. cit.*

cases, the solubility may even be increased. The solubility of certain salts, such as silver chloride,[31a] is greatly increased on addition of an electrolyte with a common ion. Since it has been shown that this effect is chiefly due to the formation of complex ions, a discussion of these systems may be omitted.

The solubility of binary salts is materially increased on the addition of a salt without a common ion. This may be accounted for on the assumption that metathetic reaction takes place between the ions of the saturating salt and the solvent electrolyte, the increased solubility being due to the formation of the corresponding un-ionized molecules. If the isohydric principle is assumed to hold for such mixtures, the resulting values obtained for the ion product and the concentration of the un-ionized salt are found to vary with the concentration of the added electrolyte in a manner similar to that found in mixtures with a common ion. Here again it is not possible to reach a conclusion relative to the nature of the processes involved with any considerable degree of certainty.

c. *The Solubility of Salts of Higher Type in the Presence of Other Electrolytes.* The solubility relations in the case of salts of higher type

TABLE CVI.

SOLUBILITY OF SILVER SULPHATE IN WATER AT 25° IN THE PRESENCE OF OTHER ELECTROLYTES.

Salt	Concentration of Salt	Solubility
None	0.00	53.52
KNO_3	24.914	57.70
	49.774	61.13
	99.87	67.93
$Mg(NO_3)_2$	24.764	59.44
	49.595	64.32
	99.46	72.70
$AgNO_3$	24.961	39.09
	49.86	28.45
	99.61	16.96
K_2SO_4	25.024	50.66
	50.044	49.35
	100.00	48.04
	200.03	48.30
$MgSO_4$	20.022	52.21
	50.069	50.93
	100.04	49.95
	200.05	49.60

[31a] Forbes, *J. Am. Chem. Soc.* 33, 1937 (1911).

are much more complex than in that of binary salts and the results are accordingly more difficult to interpret. A considerable amount of experimental material exists, much of which is due to Harkins.[32]

In Table CVI are given values of the solubility of silver sulphate in water at 25° in the presence of different electrolytes. The concentrations are expressed in millimols, $C \times 10^{-3}$, per liter. The results for this, as well as for other ternary salts, are shown graphically in Figure 53. The

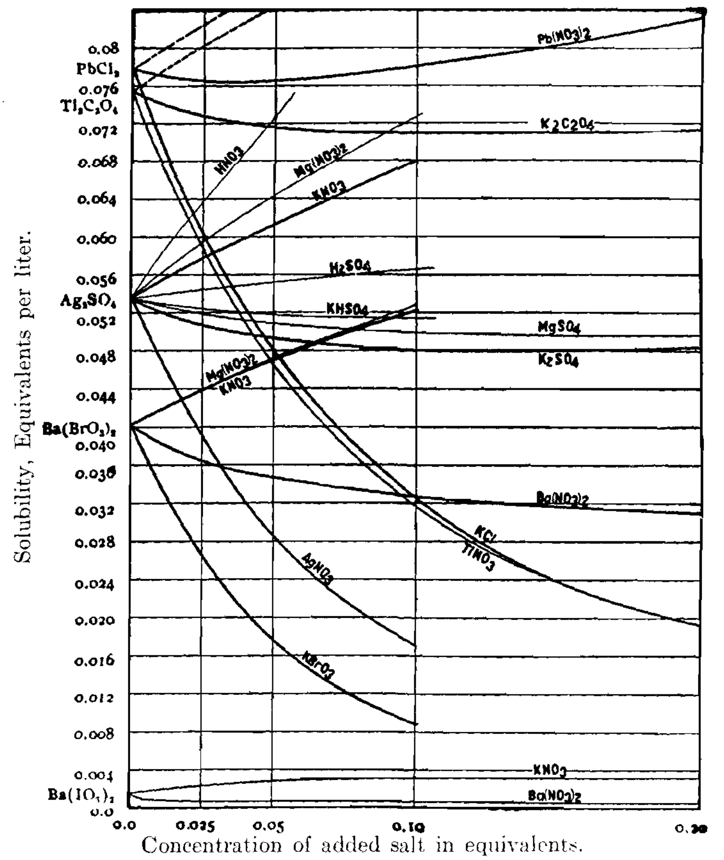

Fig. 53. Solubility of Ternary Electrolytes in Water in the Presence of Other Electrolytes.

results for lead iodate are given in Table CVII and are shown graphically in Figure 54.

An examination of the figures and the data given in the tables shows that, in general, electrolytes of the same type have a similar influence upon the solubility of a ternary electrolyte. This is particularly true

32 Harkins, *J. Am. Chem. Soc.* 33, 1807 (1911); *ibid.*, 38, 2679 (1916).

TABLE CVII.

SOLUBILITY OF LEAD IODATE IN WATER AT 25° IN THE PRESENCE OF OTHER SALTS.

Salt	Concentration Salt	Solubility
None	0.00	0.1102
$Pb(NO_3)_2$	0.1	0.087
	1.0	0.0411
	10.0	0.0185
	100.0	0.016
	500.0	0.028
	3000.0	0.150
KNO_3	2.0	0.1141
	10.0	0.1334
	50.0	0.2037
	200.0	0.2544
KIO_3	0.05304	0.0697
	0.1061	0.0437

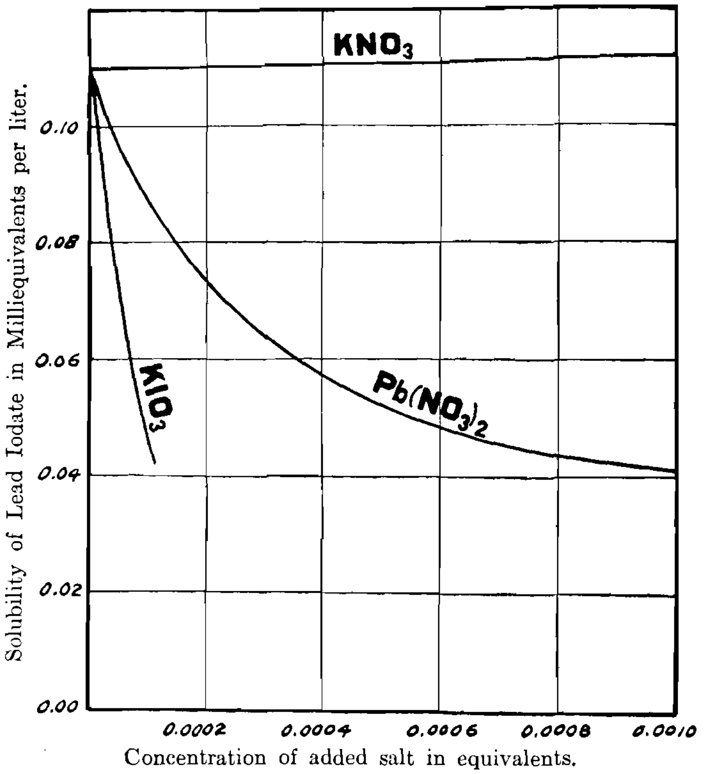

FIG. 54. Solubility of Lead Iodate in Water in the Presence of Other Electrolyte

at low concentrations. Salts having a univalent ion in common with a ternary electrolyte cause an initial depression, which, in many cases, is followed by a slight increase in the solubility at higher concentrations. This latter effect, furthermore, is greatly influenced by the properties of the electrolytes involved. The minimum is particularly pronounced in the case of solutions of lead chloride in the presence of lead nitrate. Salts which are only very slightly soluble suffer a much greater depression of the solubility on the addition of a salt with a common ion than do salts of greater solubility. The addition of an electrolyte without a common ion in general causes an increase in the solubility of a ternary salt. This increase appears to vary considerably with the nature of the added electrolyte. In the case of silver sulphate, for example, the increase in solubility due to the addition of nitric acid is much greater *than that due to the addition of potassium nitrate.*

In the case of salts whose solubility is high, the effect of an addition of various electrolytes depends largely upon the nature of the added salt. In Table CVIII are given the solubilities of strontium chloride in water

TABLE CVIII.

SOLUBILITY OF STRONTIUM CHLORIDE IN THE PRESENCE OF OTHER SALTS IN WATER AT 25°.

Salt added	Equiv. of added salt in 1000 g. H_2O	Sol. equiv. per 1000 g. H_2O
None	None	7.034
$Sr(NO_3)_2$	0.1372	7.044
	0.5766	7.038
	1.0988	7.030
	3.318	6.956
Solid $Sr(NO_3)_2$		
$NaNO_3$	0.3621	7.198
	0.5010	7.270
	3.553	7.276
	6.856	6.844
Solid $Sr(NO_3)_2$		
HNO_3	0.1771	7.028
	0.3521	7.034
	1.277	7.034
HCl	0.1551	6.882
	0.5162	6.502
	1.017	5.996
	2.165	4.864
	9.205	0.530

TABLE CVIII.—*Continued*

Salt added	Equiv. of added salt in 1000 g. H_2O	Sol. equiv. per 1000 g. H_2O
HBr	0.06817	6.974
	0.4191	6.696
	0.9716	6.262
	1.154	6.132
HI	0.1641	6.890
	0.4462	6.650
	0.4126	6.672
	0.7539	6.366
KI	0.09199	7.034
	0.5401	7.016
	0.6015	7.038
	1.445	6.992
KCl	0.0719	7.016
	0.433	6.950
	0.8576	6.882
	1.594	6.764
$CuCl_2$	0.7134	6.812
	2.276	6.352
KNO_3	0.09796	7.122
	0.4755	7.406

at 25° in the presence of different electrolytes. The results are shown graphically in Figure 55. It will be seen from the table and the figure that, up to a concentration of 1.0 N, the solubility effects are, in general, small. The difference between the effect of salts with and without a common ion is not great. The solubility of strontium chloride remains practically constant on addition of nitric acid, potassium iodide, and strontium nitrate. The addition of potassium chloride causes a slight decrease in solubility, while that of sodium nitrate causes a slight increase. The greatest decrease in solubility results from the addition of hydrochloric acid, but it is to be noted that hydriodic acid and hydrobromic acid, which do not have an ion in common with strontium chloride, cause almost as great a solubility depression as does hydrochloric acid. It is clear that, at high concentrations, the solubility effects are not to be ascribed primarily to ionic interaction. The relationships between the solubility effects resemble those obtained in the case of solutions of nonelectrolytes in the presence of electrolytes.

In the Table CIX are given values for the solubility of lanthanum

iodate in the presence of different electrolytes in water at 25°, as measured by Harkins and Pearce.[33] The results are shown graphically in Figure 56. It will be observed that the solubility of lanthanum iodate is markedly decreased on the addition of a salt with a common univalent ion. The addition of a salt with a common trivalent ion causes a slight initial decrease in solubility, followed by an increase at higher concentra-

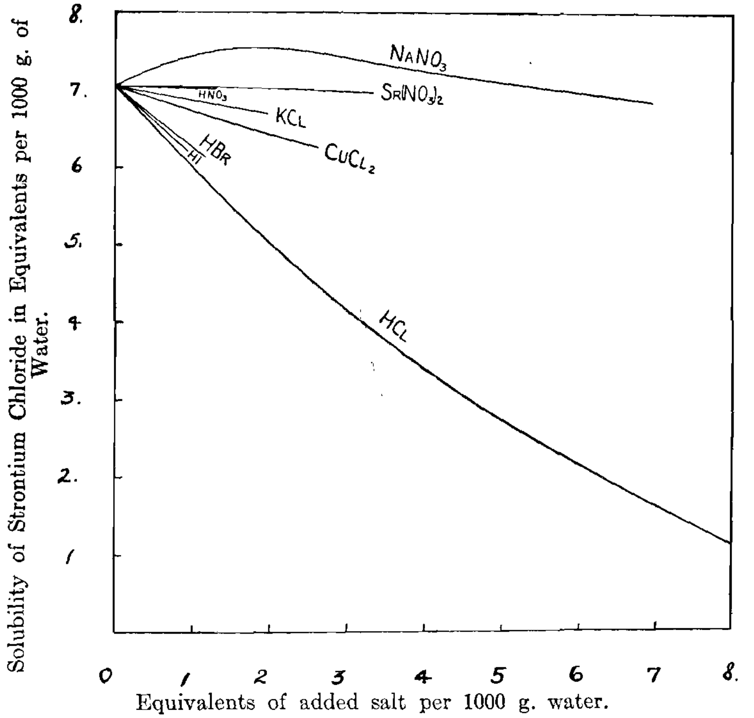

FIG. 55. Solubility of Strontium Chloride in Water in the Presence of Other Electrolytes.

tions. On the addition of a salt without a common ion, there is a marked increase in the solubility throughout.

While the solubility of different salts is in general affected in a similar manner on the addition of other salts, provided the solubility is relatively low, the interpretation of the experimental results is rendered uncertain, owing to the fact that the ionization functions for the electrolytes in the mixtures are not known. At the same time, it is possible that, in the case of salts of higher type, intermediate ions are present as a result of which it not only becomes difficult to take into account

[33] Harkins and Pearce, *J. Am. Chem. Soc.* 38, 2679 (1916).

TABLE CIX.

SOLUBILITY OF LANTHANUM IODATE IN WATER AT 25° IN THE PRESENCE OF OTHER ELECTROLYTES.

Salts added	Milli-normal conc. salt solution	Solubility in millimols
$La(NO_3)_3$	0.0	1.0301
	2.0	0.8430
	5.0	0.7968
	10.0	0.7825
	50.0	0.8320
	100.0	0.9362
	200.5	1.1195
KIO_3	0.0000	1.0301
	0.0990	0.9476
	0.4957	0.8488
	0.9914	0.7488
	1.9828	0.5632
$NaIO_3$	0.0000	1.0301
	0.0913	0.9572
	0.4560	0.8507
	0.9130	0.7658
	1.8260	0.6016
	3.6530	0.2973
	4.5326	0.2017
	6.7989	0.1468
$NaNO_3$	0.0	1.0301
	25.0	1.3092
	50.0	1.4921
	100.0	1.7481
	200.0	2.0873
	400.0	2.4657
	800.0	3.2487
	1600.0	4.3114
	3200.0	4.5657
$La(NO_3)_3.2NH_4NO_3$	0.00	1.0301
	26.34	0.9510
	52.68	1.0156
	105.36	1.1367
	158.04	1.2303
	196.83	1.3061
	393.67	1.6016
	787.35	2.0551
	1574.70	2.8968

the effect of the intermediate ion, but, in addition, the concentration of the intermediate ion cannot be determined with any degree of certainty, even in solutions in pure water. Nevertheless, as Harkins has pointed out, the solubility curves may be accounted for in a general way on the assumption that intermediate ions are present in solutions of electrolytes of higher type.

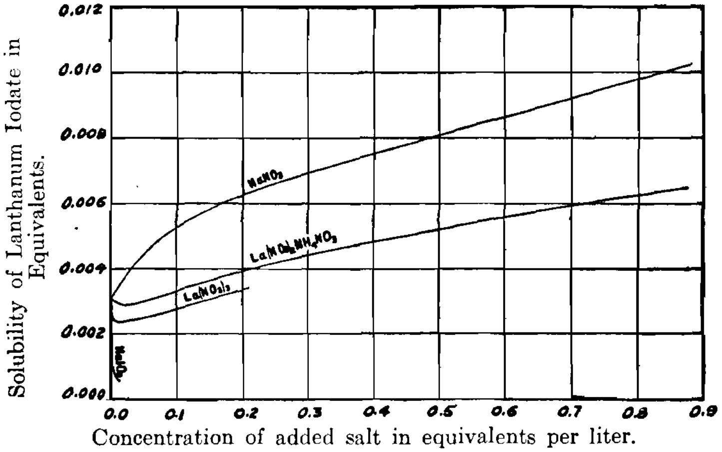

FIG. 56. Solubility of Lanthanum Iodate in Water in the Presence of Other Electrolytes.

It will be sufficient to consider, here, the solubility of a ternary electrolyte of the type MX_2, which ionizes according to the equation:

$$MX_2 = M^{++} + X^{-}.$$

As we have already seen in connection with the solubility of binary electrolytes in the presence of other electrolytes, the experimental results in the case of fairly dilute solutions are in reasonably good agreement with the assumption that the concentration of the un-ionized fraction of the salt, as well as the ion product, remains constant on the addition of other electrolytes. If a similar assumption is made in the case of a ternary electrolyte, it leads to the following equations for the solubility of the salt in the presence of an electrolyte with a common univalent ion, a common divalent ion, and without a common ion.

With a common univalent ion,

$$S = MX_2 + \frac{KMX_2}{(X^-)^2}, \tag{71}$$

where K is the ionization constant of the reaction given above. In this equation the solubility appears as an explicit function of the concentra-

tion of the common ion X^-. In order to determine the concentration of the common ion in the mixture, it is obviously necessary to know the ionization functions for the various electrolytes concerned. While these functions are not known, a fair approximation could probably be obtained by assuming one of the functions given in Chapter IX. This would necessarily involve the further assumption that intermediate ions are not present.

On the addition of a common divalent ion, the solubility is given by the equation:

$$(72) \qquad S = MX_2 + \left(\frac{KMX_2}{M^{++}}\right)^{\frac{1}{2}};$$

while, on the addition of a salt without a common ion,

$$(73) \qquad S = MX_2 + \frac{KMX_2}{(X^-)^2} + \frac{M^{++}Y^-}{K'},$$

where K' is the constant of the reaction

$$MY_2 = M^{++} + 2Y^-.$$

Since different electrolytes of the same type are ionized to practically the same extent in water, it follows that, in the mixture containing a salt without a common ion, the equivalent concentrations X^- and M^{++} will not differ greatly from each other. The first two terms of Equation 73, therefore, will remain constant on the addition of a salt without a common ion. The last term of this equation, however, will obviously increase as the concentration of the ion Y^-, due to the addition of a salt NY, increases. It is evident, therefore, that according to this equation the solubility of a ternary salt should be increased upon the addition of a salt without a common ion. On the other hand, comparing Equations 71 and 72, it is evident that the addition of a common univalent ion will cause a much greater solubility depression than will the addition of a common divalent ion, since the concentration of the univalent ion appears in the denominator with the exponent 2, while that of the divalent ion appears in the denominator with the exponent ½. Roughly, this is in agreement with observations. As may be seen by reference to Figure 53, the addition of a salt with a common univalent ion causes a much greater depression than does the addition of a salt with a common divalent ion.

As we have already seen, the solubility of a binary salt decreases as the reciprocal of the concentration of the common ion. The solubility curve of a binary electrolyte, therefore, should lie intermediate between

that of a ternary electrolyte in the presence of a common univalent ion and in that of a common divalent ion.

Harkins [34] has calculated solubility curves on the assumption that

$$(74) \qquad S^m (S + C)^n = 1,$$

where m and n are the number of ions resulting from the dissociation, while S is the solubility of the salt and C is the concentration of the added salt. The curves calculated on these assumptions correspond roughly with the observed curves. An exact correspondence is not to be expected, since the assumptions made in calculating these curves are obviously only roughly fulfilled.

The equations given above obviously do not account for the form of the curves at higher concentrations, particularly for the increase in the solubility of a ternary salt on the addition of larger amounts of a salt with a common divalent ion. According to Harkins this increase is due to the formation of an intermediate ion MX^+ according to the reaction:

$$M^{++} + X^- = MX^+.$$

On this assumption the solubility on the addition of a salt with a common univalent ion is given by the equation:

$$(75) \qquad S = MX_2 + \frac{KMX_2}{(X^-)^2} + \frac{K_1MX_2}{X^-},$$

where K_1 is the constant resulting from the reaction:

$$MX^+ + X^- = MX_2.$$

It is evident, from this equation, that, if intermediate ions MX^+ are formed, then, on the addition of an electrolyte NX, the solubility depression will be smaller than in the case where no intermediate ions are formed. From this equation, it follows, also, as may readily be seen by differentiating with respect to the concentration of the common ion X^-, that with increasing concentration the solubility must decrease irrespective of the values of the constants K and K_1.

If a salt of the type MY_2 is added, the solubility is given by the equation:

$$(76) \qquad S = MX_2 + \left(\frac{K_1MX_2}{K_2}\right)^{\frac{1}{2}} \times M^{++\frac{1}{2}} + \frac{KMX_2}{M^{++\frac{1}{2}}}.$$

Here K_2 is the equilibrium constant resulting from the reaction:

$$M^{++} + X^- = MX^+.$$

[34] Harkins, *loc. cit.*

It is evident that:

$$K = K_1 K_2. \tag{77}$$

An inspection of the above equation shows that, owing to the formation of the intermediate ion MX^+, the value of whose concentration is given by the second term of the right-hand member, the solubility is increased due to the formation of the intermediate ion. With increasing value of M^{++}, this term may become sufficiently great to overbalance the effect of the last term of the right-hand member. This is more readily seen on differentiating Equation 76 with respect to the concentration of the common ion M^{++}, which leads to the equation:

$$\frac{dS}{dM^{++}} = \frac{K^{1/2} MX_2^{1/2}}{M^{++1/2}} \left(\frac{1}{2K_2} - \frac{1}{2M^{++}} \right). \tag{78}$$

The solubility will be a minimum when:

$$\frac{1}{2K_2} = \frac{1}{2M^{++}}. \tag{79}$$

Obviously, the concentration of the common divalent ion M^{++} at the minimum point of the solubility curve is equal to the equilibrium constant K_2. If this constant is small, then the minimum point will lie at a low concentration; whereas, when this constant is large, the minimum point will lie at high concentrations. In other words, when K_2 is large the fraction of salt present in the form of intermediate ions MX^+ is relatively small; whereas when K_2 is small this fraction is relatively large and the minimum point accordingly appears at low concentrations. It may be noted, in this connection, that the solubility curves of lead salts exhibit a pronounced minimum at relatively low concentrations. That for lead iodate in the presence of lead nitrate is in the neighborhood of 0.04 N; that for lead chloride in the presence of lead nitrate is at approximately the same concentration. Silver sulphate, in the presence of potassium sulphate, exhibits a minimum in the neighborhood of 0.1 N. Calcium sulphate exhibits minima in the neighborhood of 0.15 N in the presence of salts with a common SO_4^{--} ion. In the case of salts with a common Ca^{++} ion, this minimum does not appear. The difference in the behavior of calcium sulphate in the presence of a common positive or negative divalent ion may be due to various causes, since in this case there is involved the formation of two different types of complexes. Considering the behavior of uni-divalent salts, it is evident that those salts which exhibit a pronounced tendency to form complexes, such as lead salts for example, likewise exhibit a pronounced minimum in the solubility curve in the presence of a common divalent ion.

The simple explanation offered above must obviously not be pressed too far, particularly in the more concentrated solutions. On the addition of a salt of the type MY_2, there is a possibility that complexes of the form MXY may result. In all likelihood, however, at low concentrations, these are not present to a large extent.

While solutions of highly soluble salts, as well as solutions of non-electrolytes, exhibit a great variety of properties which bring out clearly the individual characteristics of the various substances involved, in solutions of difficultly soluble salts, the solubility curves show remarkable regularities, indicating that the observed behavior of these solutions lies in properties common to electrolytes in general, at these concentrations. The solubility effects are readily explained on the assumption that the concentration of the un-ionized fraction, as well as the ion product, remains substantially constant on the addition of a second electrolyte. The great decrease in the concentration of the un-ionized fraction, which many investigators have assumed to be correct, is doubtful. It appears probable that this result follows from a failure of the applicability of the isohydric principle to mixtures of electrolytes. The solubility increase observed in the case of salts of higher type on the addition of salts with a common polyvalent ion makes it appear probable that intermediate ions are present in relatively large amounts in solutions of salts of higher type at higher concentrations.

Heterogeneous equilibria from a thermodynamic point of view will be discussed in another chapter.

Chapter XI.

Other Properties of Electrolytic Solutions.

1. *The Diffusion of Electrolytes.* If a concentration gradient exists in an electrolytic solution, diffusion will take place. The rate of diffusion of an ion is the greater the greater its mobility. However, in view of the fact that the ions of an electrolyte are oppositely charged, the diffusion of these ions will not be independent of one another. Nernst [1] has derived an expression for the diffusion coefficient in dilute solutions of electrolytes. The diffusion coefficient is thus given by the equation:

$$D = \frac{2UV}{U+V} \times RT, \tag{80}$$

in which U and V are the ionic mobilities. If the electrolyte is not completely ionized, the neutral molecules also will diffuse, and their rate of diffusion will, in general, differ from that of the ions. The diffusion coefficient of various electrolytes has been measured by Arrhenius and more extended measurements are due to Öholm.[2] In Table CX are given values for the diffusion coefficients of different electrolytes in water at 18°.

TABLE CX.

DIFFUSION COEFFICIENTS OF ELECTROLYTES IN WATER AT 18°.

Conc.	NaCl	KCl	LiCl	KJ	HCl	CH_3COOH	NaOH	KOH
0.01	1.170	1.460	1.000	1.460	2.324	0.930	1.432	1.903
0.02	1.152	1.431	0.980	1.428	2.285	0.910	1.404	1.889
0.05	1.139	1.409	0.971	1.412	2.251	0.895	1.386	1.872
0.10	1.117	1.389	0.951	1.391	2.229	0.884	1.364	1.854
0.20	1.098	1.367	0.929	1.380	2.202	0.871	1.342	1.843
0.50	1.077	1.345	0.919	1.372	2.188	0.856	1.310	1.841
1.00	1.070	1.330	0.920	1.366	2.217	0.833	1.290	1.855
2.00	..	1.320	0.928	..	..	..	1.259	1.892
2.8	1.064	..	..	1.434	..	..	..	..
3.6	..	1.338	..	..	..	..	..	..
4.2	..	..	0.956	..	..	..	..	..
5.5	1.065	..	..	1.549	..	..	..	..

[1] Nernst, *Ztschr. f. phys. Chem.* 2, 613 (1888).
[2] Öholm, *Ztschr. f. phys. Chem.* 50, 309 (1905); *Meddel. Vet.-Akad's. Nobelinstitut*, Vol. 2, No. 22 (1911).

It will be observed that in the more dilute solutions the diffusion coefficient is the greater, the greater the conductance of the electrolyte. Thus, at 0.01 normal, the diffusion coefficient of HCl is 2.324, of KOH 1.903, of KCl 1.460, and of LiCl 1.000. As the concentration increases, the diffusion coefficient in the more dilute solutions decreases. This may be accounted for if we assume that as the concentration increases the ionization decreases, and that the diffusion coefficient of the neutral molecules is smaller than that of the ions. At higher concentrations the influence of viscosity change must be taken into account. In the case of most salts, the viscosity increases with increasing concentration, and it is to be expected that, owing to this factor, there will be a decrease in the diffusion coefficient at higher concentrations. The increase in the value of the diffusion coefficient at very high concentrations cannot be accounted for in this way. If, however, the ions are hydrated, then it is not improbable that at the higher concentrations, where the number of salt molecules becomes comparable with that of the number of water molecules, the degree of hydration of the ions decreases, as a result of which their mobilities may be expected to increase.

Of particular significance are the results obtained by Arrhenius[3] for the diffusion of electrolytes in the presence of other electrolytes. If the diffusing electrolyte has a rapidly and a slowly moving ion, the diffusion of the rapidly moving ion is hindered, owing to the drag exerted upon it by the charge on the more slowly moving ion. If, now, another electrolyte is added, the rate of diffusion of the first electrolyte will be increased, since the diffusion of the oppositely charged ion may be compensated by the diffusion of another ion in the opposite direction. For example, the diffusion coefficient of a 0.52 N solution of HCl in water at 12° is 2.09, while that of the same electrolyte in 3.43 N solution of NH_4Cl is 4.67, and in a 0.375 N solution of KCl 3.89. Evidently, on adding ammonium chloride to the hydrochloric acid solution, the rate of diffusion is greatly increased due to the fact that the motion of the Cl^- ions in the direction of the concentration gradient is compensated by a motion of the NH_4^+ ions in the opposite direction. This phenomenon is quite general, as may be seen from Table CXI.

The influence of the added electrolyte on the diffusion coefficient is extremely marked. For example, the addition of 0.028 N KCl to a 1.04 N solution of HCl raises the diffusion coefficient from a value of 2.09 to 2.27, or approximately ten per cent. Effects such as these afford perhaps the strongest grounds we have for believing that electrolytes are ionized. On the other hand, they do not enable us to determine to what extent

[3] Arrhenius, *Ztschr. f. phys. Chem.* 10, 51 (1892).

TABLE CXI.

DIFFUSION COEFFICIENTS OF ELECTROLYTES IN THE PRESENCE OF OTHER ELECTROLYTES IN WATER AT 12°.

Diffusing Electrolyte	Added Electrolyte	Diffusion Coefficient at 12°
1.04-n HCl	None	2.09
"	0.67-n NaCl	3.51
"	0.1-n NaCl	2.50
"	0.75-n KCl	4.22
"	0.25-n KCl	3.08
"	0.085-n KCl	2.51
"	0.028-n KCl	2.27
"	0.75-n $BaCl_2$	4.12
"	0.085-n $BaCl_2$	2.46
"	2-n NH_4Cl	4.50
"	0.25-n NH_4Cl	2.99
0.52-n HCl	None	2.09
"	0.042-n KCl	2.46
"	0.375-n KCl	3.89
"	3.43-n NH_4Cl	4.67
0.55-n HNO_3	None	1.91
"	0.1-n KNO_3	2.59
"	0.5-n KNO_3	3.70
"	0.5-n $NaNO_3$	3.39
0.54-n NaOH	None	1.15
"	0.25-n NaCl	1.90
"	0.067-n NaCl	1.51
"	0.25-n Na_2SO_4	1.80
"	1-n $NaNO_3$	2.20
"	1-n $NaC_2H_3O_2$	1.78
"	0.2-n $NaNO_3$	1.80
"	0.2-n $NaC_2H_3O_2$	1.60
"	3-n NaCl	1.98
"	1-n NaCl	2.30
0.98-n KOH	None	1.72
"	0.1-n KCl	1.92
"	1-n KCl	2.57
0.49-n KOH	None	1.70
"	0.05-n KNO_3	1.91
"	0.5-n KNO_3	2.54
"	0.5-n KCl	2.57

ionization has taken place in a given solution. These facts, while they do not enable us to distinguish between partial and complete ionization, supply abundant evidence that salts are ionized to a large extent.

2. *Density of Electrolytic Solutions.* According to the ionic theory, the properties of dilute solutions of electrolytes are additive functions of the concentrations of the ions and of the un-ionized molecules. If π is the value of a given property of such solutions and

$$\Delta\pi = \frac{\pi - \pi_0}{C\pi_0} \times 100, \tag{81}$$

then:

$$\Delta\pi = A\gamma + B(1 - \gamma), \tag{82}$$

where π_0 is the value of the property at zero concentration, π is its value at the concentration C, γ is the ionization of the electrolyte at this concentration, and A and B are constants relating to the ions and the un-ionized molecules respectively. $\Delta\pi$ is evidently the percentage equivalent property change due to the electrolyte at the concentration in question. In applying this equation, it is tacitly assumed that the property is independent of any interaction between the ions and the un-ionized molecule, otherwise a term should be added involving the concentration and the equation would no longer be linear. Equation 82 may evidently be written:

$$\Delta\pi = B + A'\gamma, \tag{83}$$

where

$$A' = A - B. \tag{84}$$

$\Delta\pi$ is thus a linear function of γ, and from the known values of $\Delta\pi$ the values of γ may be obtained. Such additive properties lend themselves to a determination of γ, and a comparison with the value of γ as derived from conductance measurements might be expected to thus serve as a check on the correctness of these values. A simpler method of comparison consists in plotting the measured values of $\Delta\pi$ against those of γ as derived from conductance measurements.[4] If the two methods yield concordant values of γ, the graph should be a straight line.

Unfortunately, this method of checking the results of conductance measurements is restricted in its application owing to the fact that in many cases the value of a given property for the un-ionized fraction does not differ appreciably from the sum of those of its constituent ions. This appears to be the case, for example, with many of the optical properties of electrolytic solutions.

Many properties of atomic and molecular complexes depend upon the

[4] Heydweiller, *Ann. d. Phys.* *37*, 739 (1912); *ibid.*, *30*, 873 (1909); Magie, *Physical Review* *25*, 171 (1907).

number and the distribution of the charges within these complexes. If these complexes are relatively stable, as we know the ion complex to be, then the properties of the complexes will be relatively independent of the manner in which two or more of them are grouped together. We should not, therefore, expect any considerable change in those properties of electrolytes which depend primarily upon the distribution of the charges on the ions; for the ionic complexes exist practically unchanged in the un-ionized molecules whatever their state; that is, whether in solution or as liquid, solid, or, perhaps, even vapor. Only such properties as depend on the field due to the ions may be expected to exhibit a marked difference for the ions and the un-ionized molecules. In the un-ionized state the two ions form an electrical doublet with a closed field, while in the ionized state the field is open. Those properties, therefore, which depend upon the field in the immediate neighborhood of the ions should give evidence of the existence of the ions and of the un-ionized molecules, should these molecules be present in solution.

Foremost among the properties of this class we should expect the density of solutions to be included. It is well known that the solution of salts in water is accompanied by a marked volume contraction, which is the greater the lower the concentration of the solution. According to Drude and Nernst,[5] a volume change is to be expected as a result of the action of the ionic charge on the molecules of the surrounding medium. Obviously, other effects may come into play, such as the hydration of the ions, etc.

The density of aqueous solutions has been studied from this point of view by Heydweiller.[6] He found that, with a few exceptions, the density change of electrolytic solutions may be represented as a linear function of the ionization corresponding to Equation 82. It is true that the precision of the density measurements is not always great and often the concentration range over which the equation has been tested is not large. Then, again, the lowest concentrations up to which the relation has been tested is not much below 0.1 N. It is a remarkable fact, however, that for a number of electrolytes the density may be expressed as a linear function of the ionization over large concentration ranges, as, for example, in the case of zinc chloride, calcium chloride and potassium hydroxide.

The constant B is the equivalent percentage density change due to the un-ionized salt. If it be assumed that the un-ionized molecules in the solution occupy the same volume as they do in the pure condition as salts, then the value of the constant B may be calculated from the known den-

[5] Drude and Nernst, *Ztschr. f. phys. Chem.* 15, 79 (1894).
[6] Heydweiller, *loc. cit.*

sity of the salt. In Table CXII are given values of B_c, so calculated, together with values of B_e, as experimentally determined by Heydweiller for different salts in water.

TABLE CXII.

COMPARISON OF EXPERIMENTAL AND CALCULATED VALUES OF B.

Salt	B_e	B_c	Salt	B_e	B_c
NH_4I	8.38	8.55	$LiNO_3$	3.71	4.02
$NaCl$	3.36	3.15	$LiCl$	2.06	2.17
$NaNO_3$	4.88	4.74	NaI	10.45	10.77
KNO_3	5.21	5.30	1/2 CaI_2	11.55	11.70
1/2 K_2SO_4 ...	5.73	5.45	1/2 $BaBr_2$ ...	11.80	11.75
$KClO_3$	6.73	7.00	1/2 BaI_2	15.56	15.58
$AgNO_3$	13.28	13.04	1/2 $CdNO_3$ ..	9.21	9.15

From an inspection of the table it appears that the values of B_e and B_c are in remarkably good agreement. The differences probably do not exceed the experimental error. The values calculated in this way, however, do not in all cases agree as well as those appearing in the above table. In the case of salts which show a marked tendency to form hydrates, Heydweiller has employed the density of the hydrated salt rather than that of the anhydrous salt and has obtained excellent agreement between the observed and the calculated values of the constant B, while in another group of electrolytes the values of B as calculated are not in close agreement with those as measured. This is illustrated in the following table.

TABLE CXIII.

COMPARISON OF EXPERIMENTAL AND CALCULATED VALUES OF B.

Salt	B_e	B_c	Salt	B_e	B_c
NH_4Cl	0.42	1.83	KCl	2.94	3.71
NH_4Br	4.45	5.69	KBr	6.65	7.48
NH_4NO_3	2.60	3.39	KI	10.56	11.20
1/2 $N_2H_8SO_4$.	2.49	2.87	$KCNS$	3.70	4.57
LiI	9.53	10.10	1/2 K_2CrO_4 ..	5.83	6.16
$LiBr$	5.84	6.19	$RbCl$	6.24	7.79
			$CsCl$	10.36	12.62

While there is a marked deviation between the values of B as derived from the experimental curves and as calculated from the density of these

salts, nevertheless, the parallelism existing between the two sets of values is unmistakable.

The constants A are the equivalent percentage density changes due to the ions. This property should be an additive one. If this is true, the difference in the values of the constant A for salts with a common ion should be constant. Heydweiller has calculated the value of the constants A for different ions. To illustrate how nearly the additive condition is fulfilled by the experimental values of the constants, the following values are given. Table CXIV–A relates to a series of sodium salts and Table CXIV–B to a series of nitrates. In the first column is given the symbol of the negative ion of the salt, in the second column the experimentally determined value of the constant A, in the third column the value of the constant A_a for the anion, and in the last column the difference $A - A_a = A_k$ for the cation. In the case of the nitrates similar values are given for those salts.

TABLE CXIV,

SHOWING THE ADDITIVE NATURE OF A.

A. Sodium Salts

	A	A_a	A_k
$C_2H_3O_2$.	4.44	3.04	1.40
F	4.56	3.16	1.40
ClO_3	7.33	5.95	1.38
NO_3	5.95	4.54	1.41
Cl	4.38	3.02	1.36
Br	8.08	6.68	1.40
I	11.52	10.27	1.25
OH	4.88	3.40	1.48
1/2 SO_4	7.09	5.77	1.32
1/2 CrO_4	7.72	6.38	1.34
		Mean	1.38

B. Nitrates

	A	A_a	A_k
H	3.47	—1.05	4.52
Li	4.20	—0.35	4.55
Na	5.95	1.38	4.57
Ag	14.61	10.02	4.59
NH_4	3.61	—0.98	4.59
K	6.72	2.10	4.62
Rb	10.75	6.32	4.43
1/2 Mg .	5.82	1.33	4.49
1/2 Zn ..	8.09	3.61	4.48
1/2 Cd ..	9.94	5.43	4.51
1/2 Cu ..	8.14	3.63	4.51
1/2 Ca ..	6.57	2.02	4.55
1/2 Sr ..	8.98	4.38	4.60
1/2 Ba ..	(10.76)	6.54	(4.22)
1/2 Pb ..	14.87	10.34	4.53
		Mean	4.54

It will be noted that the values of the constants A_a and A_k show remarkably small variations. They thus fulfill the condition of additivity.

Only a few electrolytes, such as magnesium sulphate, sodium car-

bonate, and sulphuric acid, exhibit density changes which do not vary as linear functions of the ionization. The cause of the variation in these cases is uncertain, but may be due to the formation of complex ions, to hydrolysis, etc.

The volume changes of electrolytic solutions in methyl alcohol have likewise been examined.[7] The results obtained correspond very closely with those obtained in the case of aqueous solutions. The density change due to ionization, which is obviously equal to the difference $A - B$, is considerably greater in methyl alcohol solutions than it is in water. This is not surprising, since the dielectric constant of this solvent is much smaller than that of water. We should expect that, if the density change is the result of the action of the field due to the charge on the surrounding solvent molecules, the density change would be the greater the smaller the dielectric constant of the medium.

In order to finally establish the additive nature of the density changes of electrolytic solutions, it will be necessary to extend the measurements to much lower concentration. Methods exist for measuring the densities of dilute solutions with sufficient precision to make it possible to extend the measurements to concentrations approaching 10^{-3} N. Until this is done, the results of density measurements must remain more or less in doubt. The concordance of the results so far obtained, however, would appear to justify further efforts along these lines.

Some measurements have been made by Röhrs[8] on the density of solutions in ethyl alcohol and acetone. The interpretation of the results is uncertain owing to the small change in the ionization over the concentration intervals for which measurements were made.

3. *Velocity of Reactions as Affected by the Presence of Ions.* The speed of many reactions, such as the inversion of sugars and the hydrolysis of esters, for example, is greatly increased on addition of acids. Ostwald[9] showed that the catalytic effect of different acids is the greater the stronger the acid. It appeared, at first, that the catalytic effect of the acids provided an independent method for estimating the concentration of the hydrogen ions in an acid solution. Further investigations,[10] however, showed that the catalytic action is likewise dependent upon other factors, such as the presence of other substances and especially electrolytes. Thus, the catalytic action due to a strong acid should be reduced on the addition of a salt of this acid. While such a reduction takes place

[7] Ruthenberg, Inaugural Dissertation, Rostock (1913).
[8] Röhrs, *Ann. d. Phys.* *37*, 289 (1912).
[9] Ostwald, *J. prakt. Chem.* *28*, 449 (1883); *29*, 385 (1884); *31*, 307 (1885).
[10] Arrhenius, *Ztschr. f. phys. Chem.* *5*, 1 (1890).

in the case of the weaker acids, in that of the stronger acids the catalytic action is actually increased.

It is now commonly accepted that the un-ionized acid molecules, as well as the ions themselves, influence the rate of these reactions. According to this hypothesis, the reaction constant is given by an equation of the form:

$$K = K_i C_h + K_n C_n, \tag{85}$$

where K_i and K_n are the velocity constants for the ions and the un-ionized molecules respectively and C_h and C_n are the concentrations of the ions and the un-ionized molecules. The constant K_n is in general determined by adding, to a dilute solution of an acid, a salt of the same acid. Under these conditions, the ionization of the acid is practically repressed to zero and it is assumed that the residual catalytic action is due entirely to the un-ionized acid molecules. The results of many experiments on a great variety of reactions are, on the whole, in good accord with this hypothesis. It should be noted, however, that the ratio of the constants K_n to K_i is a function of the strength of the acid, as well as of other factors. The weaker the acid, the smaller is, in general, the value of this ratio. In the case of the strong acids, the value of this ratio may be unity or even greater.

In the following table are given values of the inversion coefficient for aqueous solutions of cane sugar, according to Ostwald, at 25°. The concentration of the acids was in all cases 0.5 N and the values given for the constants are relative to that of hydrochloric acid taken as unity.

TABLE CXV.

Inversion Coefficients for Different Acids.

Hydrochloric acid	1.000	Trichloroacetic acid	0.754
Nitric acid	1.000	Dichloroacetic acid	0.271
Chloric acid	1.035	Monochloroacetic acid	0.0484
Sulphuric acid	0.536	Formic acid	0.0153
Benzenesulphonic acid	1.044	Acetic acid	0.0040

It is clear that the catalytic action of the acids is intimately related to their strength.

For the purpose of investigating the effect of the neutral molecules upon reactions, solutions in non-aqueous solvents are in many respects better adapted than those in water, since the ionization of the acid in

these solutions is much smaller than in water. Numerous experiments have therefore been carried out in methyl and ethyl alcohols.

In the following table are given values of the esterification constant for different acids in methyl alcohol, according to Goldschmidt and Thueson,[11] at 25°. The numerical values for 0.05 HCl, 0.1 picric acid and 0.1 trichlorobutyric acid are given in the second, third and fifth columns respectively, while in the fourth and sixth columns are given the values for picric acid and trichlorobutyric acid of the strength given in the presence of 0.15 picrate and 0.1 butyrate respectively.

TABLE CXVI.

ESTERIFICATION CONSTANTS IN METHYL ALCOHOL FOR DIFFERENT ACIDS IN THE PRESENCE OF OTHER ACIDS AS CATALYZERS.

	Catalyzing acids				
Esterifying acid	HCl	$C_6H_3N_3O_7$	Picrate	$C_4Cl_3H_5O_2$	Butyrate
Phenylacetic acid ..	2.23	0.265	0.047	0.0167	0.00102
Acetic acid	4.86	0.590	0.100	0.0375	0.00172
n-Butyric acid	2.23	0.277	0.0535	0.0177	0.00097
i-Butyric acid	1.55	0.196	0.0353	0.0129	0.00074
i-Valeric acid	0.583	0.0735	0.00144	0.00475	0.00029

From this table it may be seen that the catalytic action of an acid is the greater the stronger the acid. Nevertheless, the catalytic action of an acid is not proportional to the concentration of the hydrogen ion. The ratio between the velocity constants for 0.05 N hydrochloric acid and 0.1 N picric acid varies between 7.78 and 8.91 for the different acids, while the ratio of the ion concentrations is 6.56. So, also, the ratio of the hydrogen ion concentrations for 0.1 N and 0.01 N picric acid is 3.64. The ratio of the esterification constants between these concentrations is 3.90. It will be observed that, on the addition of sodium picrate to picric acid, the velocity constant varies approximately in the ratio of 1 to 6, while, on the addition of trichlorobutyrate to butyric acid, the velocity constant changes in the ratio of 1 to 18. It should be stated in this connection that the values given for the constants of picric acid and trichlorobutyric acid in the presence of other salts represent practically the minimum limiting values which are independent of the concentration of the added salt. In other words, the salt added is sufficient to completely repress the ionization of the acid. Accordingly, the residual catalytic action of the acid must either be due to the un-ionized molecule or to some other agency. The weaker the acid, the smaller, relatively, is the

[11] Goldschmidt and Thueson, *Ztschr. f. phys. Chem.* 81, 30 (1913).

catalytic power of the neutral molecule. The values of the constants K_i and K_n may be determined from a series of measurements. In the case of the examples given above the following values of K_iC_h were obtained for trichlorobutyric acid as catalyzer at concentrations of 0.1 and 0.05 N.

TABLE CXVII.

VELOCITY COEFFICIENTS FOR THE HYDROGEN ION OF TRICHLOROBUTYRIC ACID IN THE ESTERIFICATION OF DIFFERENT ACIDS.

Concentration of Acid	Phenyl-acetic	Acetic	n-Butyric	i-Butyric	i-Valeric
0.1	0.0157	0.0358	0.0167	0.0122	0.00448
0.05	0.0109	0.0247	0.0114	0.00826	0.00304
Ratio	1.44	1.45	1.47	1.48	1.47

It is seen that the ratio of the velocity coefficients calculated for the ions between 0.1 and 0.05 N is 1.46. According to conductance measurements the ratio of the ionization of this acid at these two concentrations is 1.42. Taking into account the numerous possible sources of error, the agreement appears fairly satisfactory.

In the following table are given values of K_n and $\frac{K_n}{K_i}$ for hydrochloric acid, acetic acid, and the chloro- substitution products of this acid.[12]

TABLE CXVIII.

VARIATION OF THE RATIO $\frac{K_n}{K_i}$ FOR DIFFERENT ACIDS.

Acid	K_n	$\frac{K_n}{K_i}$	K_a
Hydrochloric acid	780	1.77	....
Dichloroacetic acid	220	0.50	5.1×10^{-2}
α-β-Dibromopropionic acid	67	0.152	1.67×10^{-2}
Monochloroacetic acid	24.5	0.055	0.155×10^{-2}
Acetic acid	1.5	0.0034	0.0018×10^{-2}

Similar results have been obtained by Taylor and by Ramstedt.[13] It is clear that the value of K_n increases with the strength of the acid. As

[12] Dawson and Powis, *J. Chem. Soc. 104*, 2135 (1913).

[13] Taylor, *Meddel K. Vet.-Akad's. Nobelinstitut*, Vol. 3, No. 1 (1913); Ramstedt, *ibid.*, Vol. 3, No. 7 (1915).

shown in the table, the catalytic action of the neutral molecule of hydrochloric acid is greater than that of the hydrogen ion. As the acids become weaker, however, the catalytic activity of the neutral molecule diminishes and reaches very low values in the case of weak acids. According to Taylor, the ratio $\frac{K_n}{K_i}$, is related to the ionization constant of the acid by the equation:

$$\left(\frac{K_n}{K_i}\right)^2 = AKa, \tag{86}$$

where A is a constant. If the law of mass action applies to the acid, this leads to the relation:

$$K_n C_u^{\frac{1}{2}} = K_i C_i,$$

where C_u and C_i are the concentrations of the un-ionized and the ionized fractions of the acid, respectively.

Many reactions are likewise catalyzed by the hydroxyl ions and, in alcohol solutions, by the alcoholate ion.[14] Since the results obtained in these cases do not differ materially from those obtained in the case of acids, the details need not be given here.

It is evident that the catalytic action of the hydrogen and hydroxyl ions may not be safely employed for determining ion concentrations. At all events, the interpretation of the results obtained is still very uncertain. In this connection, it may be noted that Arrhenius[15] has proposed an alternative hypothesis to account for the effect of the un-ionized fraction according to which the change in the catalytic activity is a secondary effect due to a change in the osmotic pressure of the molecules as a consequence of the addition of the neutral salt. While the catalytic effects due to the ions are of great interest and often of much practical importance, nevertheless, at the present time, they have not enabled us to gain any great insight into the nature of electrolytic solutions.

Recently a number of investigators have ascribed the effect of neutral salts on the catalytic action of strong acids to the influence of the added salt on the thermodynamic potential; or, what is equivalent, the activity of the hydrogen ion. Harned[16] has studied the action of neutral salts on the rate of various reactions which are catalyzed by ionic catalysts and has compared this effect with the change in the activity of the catalyzing

[14] Acree, numerous articles in the *Am. Chem. J.* and *J. Am. Chem. Soc.* since 1907. See: Acree, *Am. Chem. J.* *49*, 474 (1913).
[15] Arrhenius and Andersson, *Meddel K. Vet.-Akad's. Nobelinstitut 3*, No. 25 (1917).
[16] Harned, *J. Am. Chem. Soc.* *40*, 1461 (1918).

ions due to the addition of another salt with a common ion. He finds, in general, a correspondence between the two effects. Harned has also pointed out that the neutral salt effect appears to be related to the hydration of the added salt.

Akerlöf[17] has measured the influence of acids on the rate of reaction of ethyl acetate in water at 20° in the presence of varying concentrations of salts having an ion in common with the acid. The activity of the hydrogen ion in the presence of an added salt was determined by measurement of the electromotive force of concentration cells. With hydrochloric and sulphuric acids, Akerlöf found that, with increasing activity of the hydrogen ion, the velocity constant increases. For the same concentration of the catalyzing acid, the velocity constant K_r was found to increase approximately as the cube root of the activity of the hydrogen ion; or,

$$K_r = Aa^{\frac{1}{3}}, \tag{87}$$

where K_r is the velocity constant of the reaction, A is a constant having the same value for different salts, and a is the activity of the hydrogen ion in the mixture. In the case of a number of salts the value of A was found to depend upon the nature of the salt as well as upon its concentration. It is possible that these discrepancies are due to various sources of error. With increasing acid concentration, the constant A was found to increase, but apparently not in direct proportion to the concentration.

Equation 87 is an empirical one, and, so long as it lacks a theoretical foundation, the interpretation of the foregoing results remains uncertain. It appears that, for a number of salts, the velocity constant varies in a similar manner with the activity of the catalyzing ion; but, in view of the possible exceptions which have been found, it would be unsafe to generalize the results obtained. Further investigations along this line, however, are of considerable interest.

4. *Optical Properties of Electrolytic Solutions.* Among the various optical properties of solutions, only the absorption spectra have been determined with sufficient precision to make it possible to draw conclusions with any degree of certainty. Since the optical properties are primarily dependent upon the number and arrangement of the electrons, it is not to be expected that the ions and the un-ionized molecules will exhibit any marked difference with respect to these properties. It is true that, in the case of a few solutions, such as the copper salts for example, marked changes take place in the optical properties as the concentration

[17] Akerlöf, *Ztschr. f. phys. Chem.* 98, 360 (1921).

hanges, but these changes are to be ascribed, primarily, to a displacement of the hydration equilibrium existing in these solutions. As the olutions become more dilute, this effect disappears. The absence of any lifference in the optical effects of the ions and of the un-ionized molecules ıas led some writers to infer that un-ionized molecules are entirely wanting in electrolytes. This inference, however, does not appear to be well ounded.

In general, if no reaction takes place which tends to alter the nature of the chromophore group, the absorption of an ion is independent of the ıature of the solution, as well as that of other ions with which it may be combined. This is well illustrated in the case of the absorption of acetic ıcid in the ultra-violet region.

In Figure 57 is shown the absorption curve for acetic acid[18] in water ınd in petroleum ether and for the potassium and barium salts of this ıcid in water. From an inspection of the figure it is evident that the ıbsorption of these solutions is the same within the limits of experimental rror. In Figure 58 is shown the absorption curve for ammonium, potassium, barium and calcium salts of trichloroacetic acid in water.[19] Here, ıgain, it is evident that the absorption curves are identical within the imits of the experimental error. What holds true in the cases which ıave just been cited holds true also in solutions of other electrolytes. In general, whenever a variation arises in the absorption curve, as a result of a change in the solvent or a change in the accompanying ion, this effect may be ascribed to some reaction taking place in these solutions which alters the nature of the chromophore group.

In the following table are given the extinction coefficients for chromic ıcid and potassium bichromate in water according to the measurements of Hantzsch.[20]

TABLE CXIX.

EXTINCTION COEFFICIENTS OF CHROMIC ACID AND POTASSIUM BICHROMATE IN WATER.

		$H_2Cr_2O_7$				$K_2Cr_2O_7$		
Wave Lengths	405	436	486	543	405	436	486	546
V 10	..	..	..	1.9	..	..	..	1.73
100	..	..	89	1.8	..	291	88.7	1.67
500	333	275	..	..	..	292	86.8	..
1000	320	269	88.5	..	332	287	87.2	..

[18] Hantzsch, *Ztschr. f. phys. Chem.* 86, 629 (1914).
[19] *Idem, loc. cit.*
[20] *Idem, Ztschr. f. phys. Chem.* 63, 370 (1908).

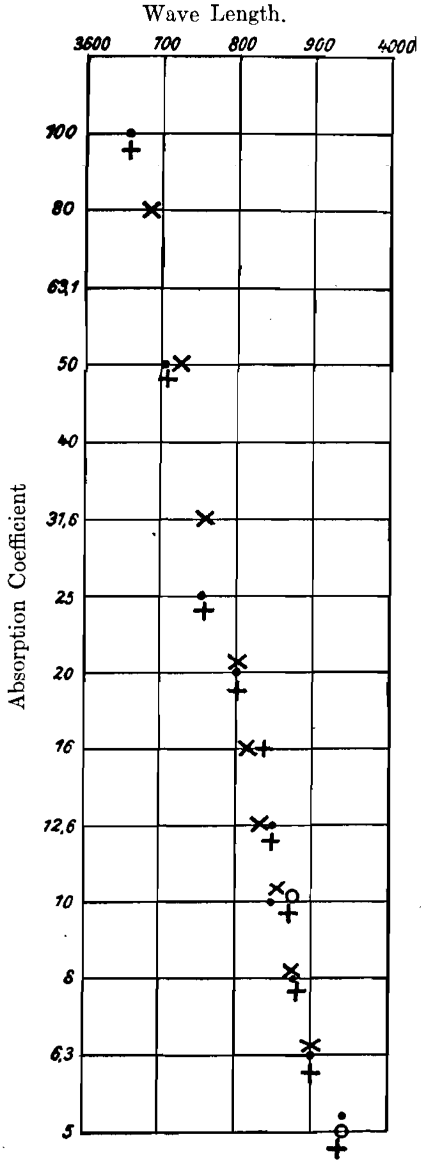

FIG. 57. Absorption Curve of Trichloroacetic Acid in Water(.) and in Petroleum Ether (×), and of Potassium Trichloroacetate in Water (+), and Barium Trichloroacetate in Water(o) as a Function of the Wave Length.

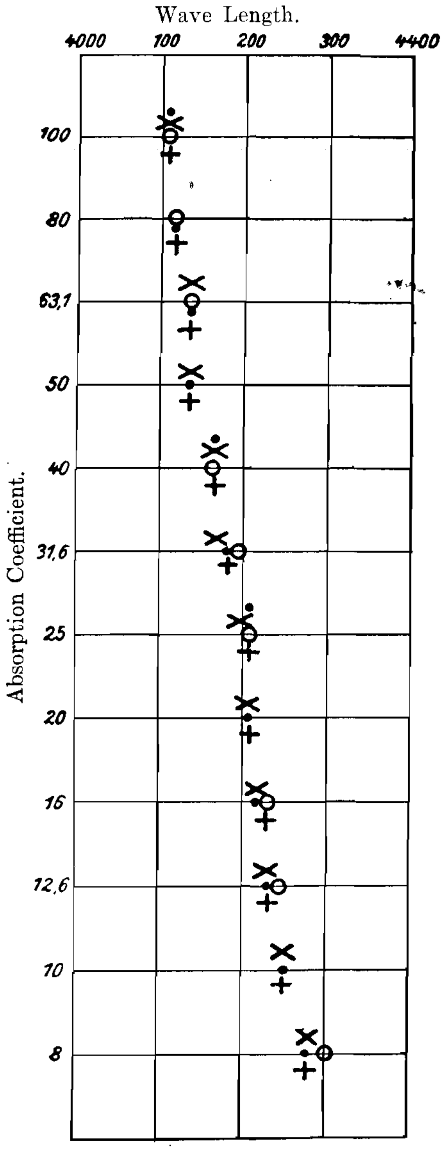

FIG. 58. Absorption Curves of Aqueous Solutions of NH_4(.), K(+), Ba(×), and Ca(o) Trichloracetates.

It will be observed, from this table, that the values of the extinction coefficients for chromic acid and potassium bichromate are identical within the limits of experimental error. The absorption here is due to the negative ion. It will be noted that the absorption, moreover, is independent of the concentration, which indicates that the negative ion in the un-ionized molecules possesses the same optical properties as in its free state; that is, in its conducting state. The absorption coefficients of the chromate ion are not affected by the presence of acid, but they are slightly affected by the presence of bases. In the following table are given values of the extinction coefficients for potassium bichromate in the presence of varying amounts of potassium hydroxide for the wave length $\lambda = 486$.

TABLE CXX.

Absorption Coefficients of Solutions of Potassium Bichromate in the Presence of Potassium Hydroxide.

Wave Length $\lambda = 486$.

Conc. Base		0	1/2000	1/100	1/1
V	50	89.9	84.3	83.7	81.7
	100	89.0	84.0	83.0	82.3
	200	89.0	83.6	82.0	81.4

It will be observed that, on the addition of potassium hydroxide, the absorption of potassium bichromate is affected to a small but measurable extent. Hantzsch has shown that this is due to the formation of other chromophore groups.

In different solvents, the chromates have identical values of the absorption coefficients, as may be seen from the following table.

TABLE CXXI.

Absorption Coefficients of Sodium Chromate in Methyl Alcohol and in Water.

$\lambda = 486$.

V	H_2O	CH_3OH
2000	229	231
5000	227	233

The results obtained from a study of other chromophore groups are similar to those obtained in the case of the chromates, and need not be given here.

Hantzsch[21] has also studied the absorption of salts of certain organic chromophore groups. In certain of these salts, marked changes have been found and Hantzsch has been able to show that in these cases the change is due to a shift in the equilibrium between two chromophore groups. In the case of salts of certain organic chromophores, however, small differences have been found for which an adequate explanation has not thus far been given.[22] In the following table are given values for the equivalent extinction coefficients for different salts of acetyloxindon.

TABLE CXXII.

EXTINCTION COEFFICIENTS FOR DIFFERENT SALTS OF ACETYLOXINDON IN WATER.

$\lambda = 436.$

Concentration:	1/100	1/250	1/1250	1/2500	1/5000
Thickness of layer:	1 mm.	1 cm.	2 cm.	5 cm.	10 cm.
Salt: Sr	..	400	388	390	384
Li	..	347	350	358	350
Na	388	385	390	382	380
Cs	383	391	387	380	390
Tl	389	385	381	390	394

In aqueous solutions, the absorption spectra of the different salts of this acid are very nearly identical with the exception of the lithium salt, whose values appear to be a little low. In the case of all salts, the extinction coefficient is independent of the concentration.

While the extinction coefficients for the oxindon salts in aqueous solutions are the same for all cations, with the possible exception of lithium, in solutions in ethyl alcohol a marked difference has been found. In Table CXXII are given values of the extinction coefficients of different salts in ethyl alcohol. It will be observed that here, again, the value of the coefficient is independent of the concentration, but that it varies with the nature of the positive ion. This variation is unquestionably far in excess of any probable experimental error. The difference might be ascribed to a difference in the optical properties of the un-ionized molecules, and it is known that in these solutions the ionization of these salts is relatively low. However, over the concentration ranges in question, the ionization for a given salt varies considerably, which makes it difficult to account for the constancy of the coefficient at different concentrations. While Hantzsch is

[21] Hantzsch, *Ber.* *43*, 82 (1910).
[22] *Idem*, *Ztschr. f. phys. Chem.* *84*, 321 (1913).

TABLE CXXIII.

EXTINCTION COEFFICIENTS FOR SALTS OF ACETYLOXINDON AT DIFFERENT CONCENTRATIONS IN ETHYL ALCOHOL.

$\lambda = 436.$

Concentration:	1/100	1/1000	1/1000	1/2500	1/5000
Thickness:	1 cm.	1 cm.	2 cm.	5 cm.	10 cm.
Salt: Ca	..	214	220	226	217
Sr	..	230	227	232	231
Ba	..	230	238	240	236
Li	259	263	255	250	258
Na	325	330	328	325	322
K	339	338	333	325	340
Rb	329	327	329	343	341
Cs	390	409	393	383	395
Tl	..	325	328	337	330

inclined to account for these variations on the basis of a slight rearrangement in the chromophore group, somewhat similar to that established in the case of the salts of the oximidoketones, a thoroughly satisfactory explanation of this behavior of the above solutions does not exist.

From the foregoing, it appears that, in solutions of salts which have stable chromophores, the absorption spectra are independent of the condition of the salt, and accordingly we may conclude that, whether an ion is combined or uncombined, the absorption spectrum remains unchanged. Where changes occur, reactions are to be looked for, the nature of which, however, has not been established in all cases.

5. *The Electromotive Force of Concentration Cells.* The properties of a solution are determined by the values of the variables which fix its state. If the solution is subject to the action of external forces, its properties will vary accordingly. Under such conditions the thermodynamic potential of the dissolved substance suffers a change and electromotive forces naturally arise under suitable arrangement of solutions and electrodes. Such, for example, is the case when solutions are subjected to centrifugal action.[23] We shall, however, confine ourselves here to a consideration of electromotive forces arising as a result of concentration difference. Wherever we have a surface of discontinuity between two electrolytes, or between an electrolyte and a metal, an electromotive force will in general arise.

For a system under the action of external forces, the condition for

[23] Tolman, *Proc. Am. Acad. 46*, 109 (1910).

equilibrium requires that the total potential shall be the same throughout the system. The total potential is defined by the equation:

$$M' = M + P, \tag{88}$$

where M' is the total potential of a given molecular species, M is its thermodynamic potential, and P is the potential due to the external forces. The thermodynamic potential may be expressed as a function of the concentration by means of the equation:

$$M = RT \log C + i + J, \tag{89}$$

where i is a function independent of concentration, while J is a function which, in general, involves all the independent variables of the system. For a concentration cell operating between the concentrations C_1 and C_2, we have:

$$(M^+ + M^-)_2 - (M^+ + M^-)_1 = -W, \tag{90}$$

where M^+ and M^- are the thermodynamic potentials of the ions of a given electrolyte and W is the work performed by the cell when one equivalent (or mol) of the electrolyte is carried from the first solution to the second. Introducing Equation 89, and writing for W its value in electrical units, we have:

$$-rEF = RT \log \frac{C_2^+ C_2^-}{C_1^+ C_1^-} + (\Sigma J_i)_2 - (\Sigma J_i)_1, \tag{91}$$

where $\Sigma J_i = J^+ + J^-$. F is the electrochemical equivalent, E the electromotive force, and r the number of equivalents of electricity flowing per equivalent of electrolyte transferred. The value of r depends upon the number of charges ν associated with a molecule of the electrolyte and the nature of the electrode process. For a concentration cell with transference,

$$r = \nu/N, \tag{92}$$

where N is the transference number of the ion to which the electrodes are impermeable. For cells without transference, $N = 1$. The electromotive force E is that due to the transfer of the electrolyte alone, and, if other processes are involved, the measured electromotive force must be corrected for these processes before introducing into Equation 91. At higher concentrations, in view of the fact that the ions are hydrated, solvent will be carried from a solution of one concentration to that of another. This process involves work and the electromotive force, as measured, must be corrected accordingly. In general, since the relative

hydration of the ions is not known at the concentrations in question, such corrections cannot be made. The same considerations hold true of the reactions in which the electrolyte is concerned, such as the formation of intermediate or complex ions, complex molecules, etc.

The electromotive force of a *concentration* cell may likewise be expressed in terms of the concentrations of the un-ionized fraction, which leads to the equation:

$$-rEF = RT \log \frac{C_{u_2}}{C_{u_1}} + J_{u_2} - J_{u_1}. \quad (93)$$

If the conditions of dilute systems are fulfilled, then:

$$J^+ = J^- = J_u = 0, \quad (94)$$

in which case the electromotive force of the cell may be calculated, if the concentration of the ions or of the un-ionized molecules is known. Equation 93, in this case, reduces to:

$$-rEF = RT \log \frac{C_2^+ C_2^-}{C_1^+ C_1^-}. \quad (95)$$

This is the equation first developed by Nernst.[24]

When the conditions for a dilute system are no longer fulfilled, the function J is involved in the expression for the electromotive force. This function thus measures the change in the potential of the electrolyte due to interaction between the various molecular species present in the mixture. The form of this function is not known, except in so far as it has been determined experimentally. The electromotive force of concentration cells has in many cases been employed for this purpose, since it affords a convenient and direct measure of the change in the potential of the electrolyte. In order to determine the true form of the function, however, it is necessary to know the concentrations C^+ and C^- or C_u. Except as the concentration of the ions may be determined from conductance measurements, no method appears to be available whereby the concentrations of the ions and of the un-ionized molecules in an electrolytic solution may be determined.

For practical purposes, the equation is often written:

$$-rEF = RT \log \frac{C_{S_2}^2}{C_{S_1}^2} + \Sigma J_{S_2} - \Sigma J_{S_1}. \quad (96)$$

[24] Nernst, *Ztschr. f. phys. Chem.* 2, 613 (1888).

If the electromotive forces have been determined experimentally, they may be expressed as a function of the total salt concentration C_S by means of this equation. In this case, the function J_S includes not only the change in the potential of the electrolyte due to the internal forces of the system, but it also includes a term which takes into account the change in the expression due to the substitution of C_S for C^+ and C^-.

The electromotive force of concentration cells for a great many electrolytes has been measured by various investigators.[25] Only a few examples of the results obtained will be given here to show, in a general way, the manner in which the potential of an electrolyte varies with the concentration. In Table CXXIV are given values of the electromotive force of concentration cells with hydrochloric acid as electrolyte between silver chloride electrodes.[26] The concentration of the concentrated solution is in this case throughout 0.1 N. The concentration of the dilute solution is given in the first column, in the second column is given the value of the electromotive force as measured, in the third and fourth columns are given the values $\frac{C_{i_1}}{C_{i_2}}$ and $\frac{C_{u_1}}{C_{u_2}}$, as determined from conductance measurements, and in the fifth and sixth columns the values of the same ratios as calculated from Equations 93 and 96, assuming $J = 0$.

TABLE CXXIV.

COMPARISON OF VALUES OF $\frac{C_{i_1}}{C_{i_2}}$ AND $\frac{C_{u_1}}{C_{u_2}}$ FOR HCl AS DERIVED FROM CONDUCTANCE AND ELECTROMOTIVE FORCE MEASUREMENTS.

Concentration of dilute sol.	E.M.F.	$\frac{C_{i_1}}{C_{i_2}}$	$\frac{C_{u_1}}{C_{u_2}}$	(Cal.) $\frac{C_{i_1}}{C_{i_2}}$	(Cal.) $\frac{C_{u_1}}{C_{u_2}}$
0.02	0.07617	4.78	7.76	4.57	20.9
0.01	0.10913	9.49	17.3	8.82	77.7
0.002	0.18711	46.7	112.5	41.8	1744.0

It will be observed that the calculated values of the ratio $\frac{C_{i_1}}{C_{i_2}}$ do not differ greatly from those derived from conductance measurements, but

[25] Linhart, *J. Am. Chem. Soc.* *39*, 2601 (1917); *ibid.*, *41*, 1175 (1919); Ellis, *ibid.*, *38*, 737 (1916); Noyes and Ellis, *ibid.*, *39*, 2532 (1917); Lewis, Brighton and Sebastian, *ibid.*, *39*, 2245 (1917); *Allmand and Polack*, *J. Chem. Soc.* *115*, 1020 (1919); Randall and Cushman, *J. Am. Chem. Soc.* *40*, 393 (1918); Harned, *ibid.*, *37*, 2460 (1915); Loomis, Essex and Meacham, *ibid.*, *39*, 1133 (1917); Loomis and Acree, *Am. Chem. J.* *46*, 632 (1911); MacInnes and Beattie, *J. Am. Chem. Soc.* *42*, 1117 (1920).

[26] Tolman and Ferguson, *J. Am. Chem. Soc.* *34*, 232 (1912).

that, on the other hand, the calculated values of the ratio $\frac{C_{u_1}}{C_{u_2}}$ differ enormously from those measured. The value of the ratio $\frac{C_{u_1}}{C_{u_2}}$, as determined from conductance measurements, may be somewhat in error owing to uncertainties in the value of Λ_0. Since the value of $1 - \gamma$ is relatively small, it is obvious that a small error in the value of Λ_0 will have a large effect on the value of the ratio determined from conductance measurements. Nevertheless, it is evident that the electromotive force as measured is much greater than that calculated according to Equation 95.

In the case of other electrolytes similar results have been obtained. In the following table are given values of $\frac{C_{i_1}}{C_{i_2}}$ as calculated from the electromotive force of potassium chloride concentration cells.[27] The concentrations of the solutions are given in the first two columns, the values found and calculated for the ion ratios are given in the last two columns.

TABLE CXXV.

Comparison of the Ratio $\frac{C_{i_1}}{C_{i_2}}$, as Determined from Electromotive Force and Conductance Measurements.

C		$\frac{C_{i_1}}{C_{i_2}}$ (Cond.)	$\frac{C_{i_1}}{C_{i_2}}$ (Cal.)
0.5	0.05	8.85	8.09
0.1	0.01	9.16	8.33
0.05	0.005	9.30	8.64
0.01	0.001	9.62	9.04

It is evident that the ion ratios as determined by means of conductance measurements are considerably greater than those calculated from the measured electromotive forces, assuming Equation 95 to hold. As the solutions become more dilute, the two values approach each other slowly.

The explanation of these phenomena has been the subject of much discussion. The observed fact is that, assuming the laws of dilute solutions to hold, the electromotive force of a concentration cell as

[27] MacInnes and Parker, *J. Am. Chem. Soc.* 37, 1445 (1915).

measured is smaller than that which would be calculated from the concentrations of the ions and larger than that calculated from the concentrations of the un-ionized fraction. One obvious explanation is that the conditions assumed to hold in applying the Nernst equation are not fulfilled, for this equation obviously can apply only to solutions which are sufficiently dilute so that the deviations from ideal systems lie within the experimental error. The behavior of solutions of strong electrolytes clearly shows that this condition is not fulfilled. The Nernst equation, therefore, should not apply.

On the other hand, it is possible that the ionization measured by means of the conductance ratio $\frac{\Lambda}{\Lambda_0}$ is not correct. If this is true, the concentrations of the ions are not known and it is therefore not possible to calculate the electromotive force of a concentration cell from Equation 95. In this case, we still have to take account of the fact that solutions of strong electrolytes do not fulfill the conditions of dilute solutions. Consequently, it is not possible to calculate from the electromotive force of concentration cells the concentrations of the ions in solution; for it may readily be shown, from electromotive force measurements, that the law of mass action does not apply to solutions of strong electrolytes and that, consequently, the laws of dilute solution do not apply. The ratios of the concentrations of the ions, therefore, cannot be calculated by means of the Nernst equation.

It has been suggested that strong electrolytes are completely ionized even at fairly high concentrations. In that case the function J_S in Equation 96 measures the change in the potential of the electrolyte due to interaction between the ions. Granting this assumption, the function J_S has a negative value at relatively low concentrations. With increasing concentration the value of J diminishes, passes through a minimum, and thereafter increases, passing through a value 0 and becoming positive at very high concentrations.[28]

A considerable number of measurements have been made on the electromotive force of concentration cells in which other electrolytes have been added to the solution of the electrolyte surrounding one electrode. Poma and Patroni[29] have measured the electromotive force of copper electrodes in solutions of copper salts, to which various electrolytes with a common ion had been added. Poma[30] measured the potential of the hydrogen electrode in acid solutions in the presence of other elec-

[28] The manner in which J varies is discussed further in the next chapter as is also the relation of this function to the activity.
[29] Poma and Patroni, *Ztschr. f. phys. Chem.* 87, 196 (1914).
[30] Poma, *Ztschr. f. phys. Chem.* 88, 671 (1914).

trolytes, both with and without a common ion. The results of Poma indicate a considerable change in the electromotive force due to the addition of another electrolyte. The effect varies with the concentration and also with the nature of the added electrolyte. At the higher concentrations of added salt, at any rate, the effect is greatly dependent upon the nature of the added electrolyte, the electromotive force due to the addition of a given amount of electrolyte being the greater the greater the tendency of the salt to form hydrates. The sign of the electromotive force, moreover, was found to depend upon the nature of the added electrolyte.

The results of Poma do not seem to be in good agreement with the results of other investigators who have investigated the electromotive force of similar cells. The potential of the hydrogen electrode in solutions of hydrochloric acid in the presence of varying amounts of alkali metal chlorides has been investigated by Chow,[31] who found that, keeping the total ion concentration constant, the potential of the electrode in the mixture may be calculated according to Equation 95, the total concentration of hydrogen and of chlorine being employed for the concentrations of the ions. According to this result, the function J_s remains constant in the mixture, provided the total concentration of the mixed electrolytes is maintained constant. Similar results have been obtained by Harned.[32] The results of Harned indicate that at low concentrations the function J_s has the same value for the mixture as it has for the pure electrolyte at the same total salt concentration. At higher concentrations, according to Harned's measurements, the potential of the electrolyte depends upon the nature of the added electrolyte. It was also found that the potential of the hydrogen electrode in hydrochloric acid suffers nearly the same change due to the addition of equivalent amounts of potassium chloride and sodium bromide.

As yet, experimental data in this direction are not sufficiently extensive to warrant generalizing the conclusions drawn from the investigations referred to above.

6. *Thermal Properties of Electrolytic Solutions.* It is only recently that the technique of thermal measurements has been refined to a point where data obtained with electrolytic solutions are sufficiently precise to make an inter-comparison of the various thermal properties of such solutions generally possible. Even now, accurate data are available for only a limited number of systems, as a result of which but few general

[31] Chow, *J. Am. Chem. Soc.* 42, 497 (1920).
[32] Harned, *J. Am. Chem. Soc.* 42, 1808 (1920); *ibid.*, 37, 2460 (1915).

conclusions may at the present time be reached relative to the manner in which the thermal quantities are dependent upon the various factors governing the condition of a solution.

Water, itself, is ionized, and the energy of the ionization reaction corresponds very satisfactorily with the heats of neutralization of strong acids and bases. According to the Ionic Theory, the heats of neutralization of different strong acids and bases should be the same at low concentrations, since the neutralization process under these conditions consists essentially in a combination of the hydrogen and hydroxyl ions to form water. The most reliable determination of the heats of neutralization was made by Wörmann.[33] The mean value of the heat of neutralization for hydrochloric and nitric acids with sodium and potassium hydroxides at 18° was found to be approximately 13700 calories. The heat of ionization of water is related to the ionization constant of water by means of the equation:

$$\frac{d \log K}{dT} = \frac{U}{RT^2}, \tag{97}$$

where U is the energy change accompanying the ionization of one mol of water. Noyes and his associates[34] have measured the ionization constant of water at a series of temperatures up to 218°. The heat of ionization derived from their results is in good agreement with the value found by Wörmann for the heat of neutralization. Thus at 18° Noyes finds that the value 14055 is in agreement with his experimental values. Direct determinations of the heat of neutralization of strong acids and bases at higher temperatures do not appear to exist, so that a comparison in these regions cannot be made. At higher temperatures the ionization constant of water passes through a maximum, as a consequence of which it follows that the heat of ionization changes sign.

Equation 97 is likewise applicable to the ionization process of electrolytes in water. If the ionization values are known at different temperatures, the energy change accompanying the ionization process may be calculated, assuming that the energy change accompanying the process remains constant. The equation holds true even though the conditions for dilute systems are not fulfilled, provided the concentrations entering in the equation represent the real concentrations of the molecular species in question. Thermal data of sufficient precision are not available to make it possible to determine to what extent the results of conductance measurements at different temperatures are in agreement with thermal data. In a general way, however, the results appear to be in agreement. In the case of the weak acids and bases, the order of

[33] Wörmann, *Ann. D. Phys. 18*, 775 (1905).
[34] Carnegie Publications, No. 63 (1907).

ıgnitude of the energy effects, as derived from conductance-temperature ɘasurements, agrees with those derived from the heats of dilution of lutions of weak electrolytes. The ionization constants of acetic acid d ammonia, for example, have maxima in the neighborhood of ordiry temperatures, indicating that the energy change accompanying the ıization process is zero; correspondingly, the heats of dilution of lutions of these substances have small, although uncertain, values. In neral, weak electrolytes have a greater heat of dilution than strong ɘctrolytes and, correspondingly, their ionization changes more largely th temperature.

The heats of dilution of strong electrolytes unquestionably have ry small values. Correspondingly, the ionization of strong electrolytes ordinary temperatures changes but little with temperature. The ıization of certain salts, such as magnesium sulphate, decreases arkedly at higher temperatures; and it is to be expected that solutions these salts will exhibit an appreciable heat of dilution even at relaʼely low concentrations. Experimental determinations of these quan.ies, however, are lacking. In view of the uncertainty of the thermal .ta, it cannot be stated that the commonly accepted ionic theory leads results which are in contradiction with the thermal properties of ɘctrolytic solutions.

Recently, careful determinations of the heats of dilution of a number electrolytes have been made by a number of investigators. Accordg to Randall and Bisson,[35] the heat of dilution of sodium chloride from ?8 N to zero concentration amounts to only two calories. At higher ncentrations the heat of dilution, although small, is quite marked. ıe heats of dilution of a number of salts, as well as of mixtures of lts, have been determined by Stearn and Smith,[36] and Smith, Stearn d Schneider.[37] The heats of dilution for sodium and potassium lorides were found to be very nearly the same, although varying ghtly at high concentrations. At low concentrations, the heat of diluɔn, in all cases, approaches a value of zero, as might be expected. The ats of dilution are not in all cases of the same sign, since that of ·ontium chloride is opposite in sign from that of sodium and potassium lorides. The heats of dilution for mixtures of two electrolytes in neral differs markedly from the mean heat of dilution of the contuents. Stearn and Smith suggest that this result may be due to the ct that complex compounds, whose formation presumably would be companied by an energy change, are formed in mixtures of salts. For dium and potassium chlorides the heat of dilution is negative, which

[35] Randall and Bisson, *J. Am. Chem. Soc.* 42, 347 (1920).
[36] Stearn and Smith, *J. Am. Chem. Soc.* 42, 18 (1920).
[37] Smith, Stearn and Schneider, *ibid.*, 42, 32 (1920).

corresponds to an increase in the ionization of these electrolytes with the temperature. This is not in agreement with the observed results of conductance measurements. It is possible, however, that the energy change measured on the dilution of a solution includes effects other than those due to change in the ionization of the electrolyte. Certainly, at the higher concentrations, it is to be expected that a change in the hydration of the ions, and possibly of the neutral molecules, takes place, and the energy change accompanying these processes may obscure the energy change due to the ionization process.

It appears, thus, that a knowledge of the thermal properties of electrolytic solutions has a very direct bearing on our interpretation of the phenomena observed in electrolytic solutions. In order to analyze the more or less complex processes into their constituent effects, however, further experimental data are required.

In this connection, it should also be noted that a number of investigators,[38] from a study of the temperature coefficient of the electromotive force of concentration cells, have obtained values for the energy changes accompanying the transfer of electrolytes from solutions of one concentration to another. Harned has also determined the energy changes accompanying the transfer of hydrochloric acid from a solution containing a mixture of salt and acid to one containing acid alone. Hydrochloric acid and chlorides were employed in these mixtures.

In the following table are given values of the energy change accompanying the transfer of one mol of electrolyte from the concentration given to a concentration of 0.1 N, according to Ellis and Harned.

TABLE CXXVI.

ENERGY CHANGE, IN JOULES, ACCOMPANYING THE TRANSFER OF ONE MOL OF ELECTROLYTE FROM A CONCENTRATION C TO A CONCENTRATION 0.1 N AT 25°.

C	KCl	NaCl	HCl
0.1000	000	000	000
0.3000	—355	—300	420
0.5000	—650	—570	820
1.000	—1310	—1196	1820
1.500	—1900	—1780	2770
2.000	—2375	—2300	3720
2.500	—2810	—2690	4740
3.000	—3175	—3010	5710

As may be seen from the table, the energy changes accompanying the transfer of sodium and potassium chlorides differ but little. The sign of

[38] Ellis, *J. Am. Chem. Soc.* 38, 737 (1916); Harned, *ibid.*, 42, 1808 (1920).

the energy change in the case of hydrochloric acid is opposite from that of sodium and potassium chlorides.

Harned has also determined the energy changes accompanying the transfer of hydrochloric acid from solutions containing hydrochloric acid of concentration 0.1 N, together with an added salt having a common chloride ion at varying concentrations, C, to a solution of pure hydrochloric acid at a concentration of 0.1 N. The results are given in the following table.

TABLE CXXVII.

ENERGY CHANGE ACCOMPANYING THE TRANSFER OF TWO MOLS OF HCl FROM SOLUTIONS OF 0.1 N HCl + CN MCl TO A SOLUTION OF 0.1 N HCl AT 25°.

KCl

C	0.2018	0.5086	1.0346	2.134	3.309
ΔH	6	37	149	1371	2807

NaCl

C	0.1003	0.2014	0.5061	0.9183	1.023	1.871	2.094	2.711	3.202	3.726
ΔH	—44	142	273	569	755	2373	2381	3595	4647	5942

LiCl

C	0.8485	1.7267	2.636	3.574	4.556
ΔH	1407	4128	6527	9200	11610

It will be observed that the energy change is greatest for LiCl and least for KCl. Apparently, the energy change is greatest for those salts which exhibit the greatest tendency to form hydrates. These energy changes persist below 0.1 N. This is apparently also the case in solutions of the pure electrolytes.[39]

7. *Change of the Transference Numbers at Low Concentrations.* The transference numbers of an electrolyte are determined by the relative speed of its ions. Any influence, therefore, which tends to alter the relative speed of the ions obviously tends to alter the transference numbers of the electrolyte. The speed of the ions is a function of the viscosity of the solution and, for a given change of viscosity, the change in the speed of an ion depends upon the nature of the ion. This, for example, is evident from the effect of temperature on the ionic conductances, where, as we have seen, the temperature effect is the smaller the greater the conductance of the ion. At higher concentrations, therefore, where the viscosity effect is appreciable, a change in the value of the transference numbers is not unexpected.[39a] At low concentrations, however, we should expect the transference numbers to be constant.

This condition is apparently not fulfilled in solutions of strong acids and bases. For example, the anion transference number of hydrochloric

[39] Compare Ellis, *loc. cit.*

[39a] It has been found that the transference number of lithium chloride is not altered on the addition of raffinose (Millard, Thesis, Univ. of Ill. (1914)). Reference to Table

acid in water at 18° varies from 0.168 at 0.005 N to 0.165 at 0.1 N.[40] In a sense, this does not appear to be a great change in the value of the transference number. Nevertheless, it is in excess of what might be expected from the viscosity effect in these solutions. Furthermore, the conductance of the chloride ion as calculated from the transference number and the degree of ionization does not correspond with the value of the conductance of the chloride ion at infinite dilution in solutions of potassium chloride. Assuming for the transference number of the chloride ion in hydrochloric acid the value 0.167 and for the ionization the value 0.972 and for the conductance the value 369.3 at 0.01 N and 18°, we obtain, for the conductance of the chloride ion, the value $\Lambda_{Cl} = \Lambda_{HCl} \times \frac{N_C}{\gamma_C} = \frac{369.3 \times .167}{.972} = 62.68$. At infinite dilution the conductance of the chloride ion has a value of 65.5. It appears, then, that up to a concentration of 0.01 N the conductance of the chloride ion has fallen from a value of 65.5 to a value of 62.68. This value is obviously subject to a correction, since, in calculating the value of γ by the ratio $\frac{\Lambda}{\Lambda_0}$, it has been tacitly assumed that the speed of the ions remains constant.

Noyes[41] called attention to this discrepancy which exists in the case of the strong acids. Lewis[42] showed that the ionization of different chlorides as calculated from the conductance of the chloride ion at a given concentration is the same for all chlorides. MacInnes[43] has investigated the conductance of various ions at higher concentrations in some detail. The conductance of an ion at a given concentration is obtained by multiplying the conductance of the electrolyte by the transference number of the ion in question at that concentration. In the case of the chlorides, he obtained the following results:

XLIII will show that the conductance of lithium, caesium and potassium chlorides is affected to almost the same extent on the addition of raffinose. Evidently, the viscosity change due to raffinose affects the Li^+, Cs^+ and K^+ ions to the same extent. From the same table, it is evident that the conductance of potassium chloride and lithium chloride is altered to very nearly the same extent, even on the addition of some non-electrolyte of relatively low molecular weight. In methyl alcohol, however, the exponent p is markedly larger for LiCl than for CsCl. In the presence of this non-electrolyte, the influence of viscosity on ion conductance depends upon the nature of the ion. Correspondingly, Millard (*loc. cit.*) found that the transference number of the lithium ion in lithium chloride solution is decreased from 0.322 to 0.307 on the addition of 0.4 mol of methyl alcohol per 1000 g. of water. The viscosity effect due to the electrolyte itself has an influence on the conductance of an ion which differs markedly from that due to a non-electrolyte of large molecular weight. In considering the influence of viscosity on the speed of an ion, the nature of the particles to which the viscosity change is due must not be lost sight of.

[40] Noyes and Kato, *J. Am. Chem. Soc. 30*, 318 (1908).

[41] Noyes and Sammet, *J. Am. Chem. Soc. 24*, 944 (1902); *ibid., 25*, 165 (1903); *Ztschr. f. phys. Chem. 43*, 49 (1903); Noyes and Kato, *ibid., 62*, 420 (1908).

[42] Lewis, *J. Am. Chem. Soc. 34*, 1631 (1912).

[43] MacInnes, *J. Am. Chem. Soc. 41*, 1086 (1919); *ibid., 43*, 1217 (1921).

TABLE CXXVIII.

CONDUCTANCE OF THE CHLORIDE ION AT 18° AS DERIVED FROM THE CONDUCTANCE AND THE TRANSFERENCE NUMBERS OF DIFFERENT ELECTROLYTES AT 0.01 N AND 18°.

	Λ	η	T_{Cl}	$T_{Cl}\Lambda\eta^{0.7}$
HCl	369.3	1.0005	0.167	61.67
CsCl	125.07	0.9997	0.495	61.89
KCl	122.37	0.9996	0.504	61.68
NaCl	101.88	1.0009	0.604	61.55
LiCl	91.97	1.0016	0.668	61.48

Here T_{Cl} is the transference number of the chloride ion and $T_{Cl}\Lambda\eta^{0.7}$ is the conductance of the chloride ion corrected for viscosity. From an inspection of this table, it is evident that the conductance of the chloride ion, as derived from the transference numbers and conductances of different chlorides, is the same. The ion conductances given in the last column have been corrected for the viscosity according to Equation 41, assuming for the exponent p the value 0.7. This viscosity correction is uncertain, but in view of the fact that the viscosity effect in all these solutions is scarcely in excess of 0.1 per cent it is evident that the viscosity correction can have only a minor influence. While the conductance of the chloride ion in the different chlorides is very nearly the same, it does not appear to be identical. In lithium chloride, for example, the conductance is approximately 0.7 per cent lower than it is in caesium chloride, and from caesium chloride to lithium chloride the conductances vary in the order: caesium, potassium, sodium, lithium. If the differences were purely accidental, we should not expect any such regularity in the order of the conductance values. MacInnes has also made a similar comparison at higher concentrations up to and including 1.0 N. Throughout he obtains excellent agreement among the conductance values of the chloride ion in different chlorides. It should be noted, however, that, at the higher concentrations, the viscosity effects are considerable, and the ion conductances in consequence are proportionately in doubt.

MacInnes is inclined to believe that it is generally true that at a given concentration the conductance due to a given ion is independent of the nature of other ions present in the solution. This generalization, however, does not appear to be wholly justified. For example, assuming the transference values given by Noyes and Falk, we obtain for the conductance of the nitrate ion at 0.2 N in solutions of KNO_3, $AgNO_3$

and HNO_3 the values 57.28, 55.60 and 56.40 respectively. There is, however, a considerable degree of uncertainty attached to these calculations owing to uncertainties in the values of the transference numbers. The errors with which transference measurements are affected are relatively large and it is possible that consistent errors are present, in which case the probable error of the determination cannot be estimated from the consistency of a given series of measurements. In many respects, it would appear that transference measurements by the moving boundary method should be more nearly comparable than those by other methods. In Table CXXIX are given values of the ion conductance Λ_{K^+} of the potassium ion and of $\frac{\Lambda_{K^+}}{\gamma}$ for the same ion for different potassium salts at concentrations of 0.02 N and 0.1 N. The ionization and conductance values are taken from Noyes and Falk and the transference values from Dennison and Steele.[44] The numbers in the next to the last column are the ion conductances, which should have the same value if the conductance of a given ion at a given concentration were independent of the nature of the other ion with which it is combined. In the last column are given the values of $\frac{\Lambda_{K^+}}{\gamma}$ which, if the transference number is independent of concentration and the ionization is measured by the ratio $\frac{\Lambda}{\Lambda_0}$, should correspond with the conductance of the potassium ion at infinite dilution.

TABLE CXXIX.

VALUES OF Λ_{K^+} AND OF $\frac{\Lambda_{K^+}}{\gamma}$ FOR DIFFERENT POTASSIUM SALTS.

At 0.02 N.

	T_C	γ	Λ_C	Λ_{K^+}	$\frac{\Lambda_{K^+}}{\gamma}$
KCl	0.493	0.922	119.9	59.13	64.14
KNO_3	0.502	0.911	115.0	57.78	63.44
KBr	0.482	0.921	121.7	58.68	63.72
$KClO_3$	0.534	0.910	108.8	58.12	63.88
$KBrO_3$	0.567	0.910	102.0	57.84	63.58
KI	0.487	0.922	120.9	58.90	63.90
				Mean 58.41	Mean 63.78
				A.D. 0.50	A.D. 0.20

[44] Dennison and Steele, *Phil. Trans. A*, *205*, 462 (1906).

TABLE CXXIX.—*Continued*

At 0.1 N.

	Λ_0	γ_u	Λ	Λ_{K^+}	$\frac{\Lambda_{K^+}}{\gamma}$
KCl	130.0	0.861	111.97	55.10	64.04
KNO_3	126.3	0.829	104.71	52.60	63.50
KBr	132.2	0.863	114.14	54.92	63.64
$KClO_3$	119.6	0.829	99.14	53.17	64.14
$KBrO_3$	112.1	0.829	93.0	52.98	63.93
KI	131.1	0.870	113.98	55.40	63.68
			Mean	54.03	Mean 63.82
			A.D.	1.11	A.D. 0.21

It will be observed that at 0.02 N the value of Λ_{K^+} varies from 57.78 to 59.13 with a mean deviation of 0.50, while $\frac{\Lambda_{K^+}}{\gamma}$ varies from 63.44 to 64.14 with a mean deviation of 0.20. At a concentration of 0.1 N the value of Λ_{K^+} varies from 52.60 to 55.40 with a mean deviation of 1.11, while the value of $\frac{\Lambda_{K^+}}{\gamma}$ varies from 63.50 to 64.14 with a mean deviation of 0.21. It is evident that the conductance of the potassium ion in different salts is not the same, while the ratio $\frac{\Lambda_{K^+}}{\gamma}$ is substantially the same.[45] These results, therefore, do not bear out the conclusion that the conductance of an ion is independent of the other ion with which it is combined. Leaving aside for the moment the strong acids and bases, it appears that conductance and transference measurements agree with the assumption that the conductance of a given ion varies with the nature of its co-ion and that the difference in the conduction of a given ion is proportional to the ionization of its salt. The reason why the conductance of the chloride ion is found the same for different electrolytes is due to the fact that the ionization of these electrolytes is the same at the same concentration. If corrected values of the conductance are employed, the ionization of sodium, potassium, and lithium chlorides, as determined from conductance measurements, is substantially the same up to 1.0 N. Up to a concentration where the viscosity effects begin to become appreciable there is no certain evidence indicating that the relative speeds of the ions undergo change. In the case of

[45] This conclusion was reached by Dennison and Steele (*Phil. Trans. A* *205*, 462 (1906)).

the strong acids and bases, however, the experimental data indicate that the speed of one of the ions, at least, undergoes a marked change at concentrations below 10^{-2} N. The nature of the process to which this change is due remains uncertain.

8. *Reactions in Electrolytic Solutions.* Electrolytic solutions, in water at least, are characterized by the speed with which they take place, as well as by their reversibility. This property of electrolytic solutions has been cited in support of the ionic theory; and, indeed, the reactions among electrolytes clearly indicate some common condition as a result of which they take place with great facility and, as a rule, with the accompaniment of a comparatively small energy change. It is only in a few other systems that reactions similarly take place with great speed, and many of these are irreversible. Reactions in fused salts and in the metals, however, resemble those in electrolytic solutions in many respects. There is little question but that reactions in fused salts are ionic in character. While available data are extremely meager in the case of the metals, there is evidence which indicates that here, too, reactions may be ionic.

In a few instances, in water as well as in some other solvents, solutions of electrolytes do not reach equilibrium at once when an electrolyte is dissolved. In those cases which have been studied in detail, it has been shown that intermediate reactions occur which greatly influence the properties of the solution; so, for example, certain of the metal-ammonia salts, when first dissolved in water, yield solutions which are very poor conductors of the current, but which, on standing, show a marked increase in conductance. Here, unquestionably, the gradual increase of the conductance is due to a reaction as a result of which the metal-ammonia complex is affected. The original complex is not capable of ionization, while the resulting product is ionized. These particular reactions are accounted for by Werner's theory. Aside from a few cases of this type, solutions of electrolytes reach a condition of equilibrium as soon as the process of solution is completed.

It will be unnecessary, here, to discuss reactions in aqueous solutions since these are familiar to everyone who has studied the elements of chemistry. Since solutions in non-aqueous solvents are ionized, we may expect that similar reactions take place in solutions in these solvents. The nature of the reactions will, of course, depend upon the nature of the solvent as well as upon that of the dissolved electrolytes.

The multiplicity of electrolytic reactions in aqueous solvents is in part due to the electrolytic properties of water itself. As we have seen, water is ionized to a slight extent into hydrogen and the hydroxyl ions.

When one or more electrolytes are dissolved in water, the resulting reaction is influenced by the presence of these ions due to the solvent. We should expect similar reactions in the case of all solvents capable of ionization. This includes, in the first place, solvents containing hydrogen, such as the liquid halogen acids, ammonia, hydrocyanic acid, formic acid, acetic acid, the alcohols, the amines, etc. In all these cases, it is to be anticipated that the solvent will furnish a positive hydrogen ion and a negative ion corresponding to the constitution of the solvent. The hydrogen or acid ion of substances dissolved in solvents which themselves yield a hydrogen ion will exhibit acid properties. The negative ion, correspondingly, may be considered as a basic ion and salts of this ion will act as bases when dissolved in a solvent yielding the same ion. So, in the case of the alcohols, the acids exhibit acidic properties, while the alcoholates exhibit basic properties. Similarly, in ammonia, the ammonium salts exhibit acidic properties, while the basic amides exhibit basic properties. On the other hand, a base typical of water, such as tetramethylammonium hydroxide, would properly be classed as a salt when dissolved in ammonia. However, many of the characteristic properties of acids and bases are not entirely dependent upon the presence of a positive or a negative ion in common with the solvent. For example, any salt of a strong base and a weak acid will exhibit properties characteristic of a base when in solution. Thus, tetramethylammonium hydroxide in ammonia exhibits basic properties, very similar to those of potassium amide, the reason for which lies in the fact that the resulting acid formed by the hydrolysis, or ammonolysis, of this salt in ammonia is a very weak acid water, which, as we know, is only very slightly ionized in liquid ammonia. Correspondingly, a cyanide dissolved in water exhibits basic properties for the reason that hydrocyanic acid is only slightly ionized in water. Strictly speaking, an acid has a positive ion and a base a negative ion in common with the solvent; nevertheless, salts of strong acids and very weak bases and salts of strong bases and very weak acids exhibit certain acidic and basic properties in solution.

We have seen that the OH^- ion is a characteristic basic ion only in aqueous solution and that in other solvents other ions function as basic ions. So, also, any positive ion common to a solvent will in that solvent exhibit many of the properties of an acid ion. For example, iron introduced into an aqueous solution of an acid yields a salt and hydrogen. Similarly, iron introduced into molten lead salt yields a corresponding salt of iron and metallic lead. Excepting for the fact that in the first case hydrogen is a gas and in the second case lead is a liquid metal, there is no essential distinction in the nature of the reaction in the two

cases. The number of examples of this type might be greatly multiplied.

Liquid ammonia is the only non-aqueous solvent in which electrolytic reactions have been extensively studied so that this discussion must be largely confined to solutions in this solvent. The study of reactions in ammonia have led to a considerable extension of our notions respecting electrolytic reactions in general, and have greatly advanced our knowledge regarding the nature of various nitrogen compounds. Solutions in ammonia exhibit properties similar to those of solutions in water, because of the similarity of constitution of the two solvents. In water we have the ionization reaction:

$$H_2O = H^+ + OH^-$$

and in ammonia the corresponding reaction:

$$NH_3 = H^+ + NH_2^-.$$

The negative ions in ammonia and water differ, but exhibit many points of similarity. The positive ions in the two solvents are the same and exhibit a similar behavior. In ammonia solutions, however, the hydrogen ion appears to be identical with the ammonium ion, whereas in aqueous solution the hydrogen ion is in all likelihood a complex between hydrogen and water, so that the two ions are not identical. The same is doubtless true of most ions. In their essential behavior, however, the hydrogen ions in ammonia do not differ materially from the hydrogen ions in water. One of the characteristic properties of the hydrogen ions is its tendency to react with metals to form a salt and hydrogen. In water, for example, we have the reaction:

$$Mg + 2HCl = MgCl_2 + H_2.$$

So, in ammonia we have the reaction:

$$Mg + 2NH_4Cl = MgCl_2 + H_2 + 2NH_3.$$

In this last reaction, the ammonia resulting from the reaction is identical with the solvent molecules and therefore may be omitted from the reaction equations. In aqueous solutions of the acids this is always done, for it is less evident that water is concerned in the reaction. In ammonia, the acids react with bases to form salts and water, corresponding to the reactions in aqueous solutions; thus:

$$(CH_3)_4NOH + HCl = (CH_3)_4NCl + H_2O \text{ in water,}$$

and $(CH_3)_4NOH + NH_4Cl = (CH_3)_4NCl + NH_3 + H_2O$ in ammonia.

In aqueous solutions, with a few exceptions, the acids are substances in which the hydrogen is joined to an electronegative group through an oxygen atom. For example, in the case of acetic acid we have CH_3COO^--H^+. Such acids are known as hydroxy-acids, or perhaps better aquo-acids, as Franklin has suggested. Similarly, in the case of ammonia, substances in which the hydrogen atoms are connected to an electronegative group through the intermediary of a nitrogen atom are acids. This is a class of substances commonly known as the acid amides or imides. Thus, we have, corresponding to acetic acid CH_3COOH, acetamide CH_3CONH_2. Acetamide is therefore an acid related to ammonia as acetic acid is to water, and, according to Franklin, may be called an ammono-acid.[46] In view of the fact that nitrogen is tri-valent, the acid amides are dibasic acids in contrast with the corresponding aquo-acids which are mono-basic. As we have seen in an earlier chapter, the acid amides are soluble in ammonia and many of them are excellent conductors of the electric current. It has been shown that the acid amides and imides in ammonia possess characteristic acidic properties; that is, they react with the metals to form salts and hydrogen and with bases to form salts and ammonia. Thus we have:

$$Mg + CH_3CONH_2 = CH_3CONMg + H_2,$$

a reaction similar to that obtained with acetic acid in water. The acid amides likewise react with bases in ammonia to form salts and water; for example,

$$CH_3CONH_2 + (CH_3)_4NOH = CH_3CONH(CH_3)_4N + H_2O.$$

Acid amides in ammonia solution are weaker acids than the corresponding oxy-acids are in aqueous solutions, but this is to be expected, since the dielectric constant of ammonia is much lower than that of water and the ionization of all electrolytes is lower in ammonia than in water. However, as may be seen from the conductance values for the acid amides in ammonia solution as given in an earlier chapter, the ionization of certain of these acids in ammonia is as great as that of typical salts in this solvent. Relatively, therefore, the acid amides are as strong in ammonia as ordinary acids are in water. It is interesting to point out, in this connection, that, while the acid amides throughout exhibit acidic properties in ammonia solution, it is only in exceptional cases that they exhibit marked acidic properties in water. The reason for this is not well understood, but it seems probable that, when the acid amides are

[46] Franklin, *Am. Chem. J.* *47*, 285 (1912). See also numerous other articles by the same author in the *Am. Chem. J.* and *J. Am. Chem. Soc.*

dissolved in water, the basic properties of the nitrogen come into play and that compounds of a basic nature are formed similar to ammonium hydroxide, which, however, are ionized only to an exceedingly small extent, in view of the electronegative character of the rest of the molecule.

As has already been pointed out, the basic amides, as for example potassium and sodium amides, are electrolytes in ammonia solution and, from their constitutional relation to ammonia, it is to be expected that solutions of these substances will exhibit basic properties in liquid ammonia. This is, indeed, the case. Potassium amide, dissolved in liquid ammonia, exhibits all the properties characteristic of bases. For example, it reacts with acids to form salts and ammonia; thus:

$$CH_3COOH + KNH_2 = CH_3COOK + NH_3.$$

According to Franklin, bases of this type are called ammono-bases. Obviously, all basic amides belong to this class of substances.

The ammono-bases react not only with aquo-acids but also with ammono-acids.[47] Thus, an ammono-acid reacts with an ammono-base to form an acid ammono-salt and ammonia, according to the equation:

$$CH_3CONH_2 + KNH_2 = CH_3CONHK + NH_3.$$

It is interesting to note that the color reactions characteristic of indicators are likewise found reproduced in ammonia solutions.[48] Some indicators exhibit a remarkably sharp end point; as, for example, saffranine. The nature of the indicator reactions have not, as yet, been studied in detail.

In aqueous solutions, salts of weak acids and bases are hydrolyzed owing to interaction between the ions of the solvent with those of the dissolved salt. So, also, in ammonia solutions, the salts of very weak acids and bases are ammonolyzed; that is, the salt reacts with the solvent to form an acid and a base. Unfortunately, the extent to which ammonia is ionized into H^+ and NH_2^- ions is not known. In all likelihood, however, the concentration of these ions is extremely low, since the alkali metals are soluble in liquid ammonia and remain in solution for extended periods of time with only a slight reaction, according to the equation:

$$NH_3 + Na = NaNH_2 + \tfrac{1}{2}H_2.$$

If the concentration of the hydrogen ions were considerable, this reaction should take place with great rapidity just as the corresponding reaction takes place in water. That hydrolysis (or ammonolysis) actually takes

[47] Franklin and Stafford, *Am. Chem. J.* 28, 83 (1902).
[48] Franklin and Kraus, *Am. Chem. J.* 23, 277 (1900).

place, however, has been definitely shown. As a consequence of the very low concentration of the H^+ and NH_2^- ions in ammonia, it is only in the case of salts of extremely weak acids or bases that hydrolysis has been observed. For example, when mercuric chloride is dissolved in ammonia the following reaction occurs:

$$HgCl_2 + NH_2^- + NH_3 = HgNH_2Cl + NH_4Cl.$$

In this case, the compound $HgNH_2Cl$ is insoluble and is precipitated. Obviously, this precipitation proceeds *until* the concentration of NH_4Cl is sufficiently great to bring the reaction to equilibrium. The addition of an ammonium salt, which raises the concentration of the NH_4^+ (hydrogen) ions, reverses the reaction, causing the precipitate to go into solution; while, on the other hand, the addition of an ammono-base, KNH_2, for example, results in an increased precipitation. In most instances, however, salts dissolve in ammonia without appreciable ammonolysis. This is indicated by the fact that in many cases the resulting base or basic salt is practically insoluble and even a small degree of ammonolysis would result in the formation of a precipitate. Since in the great majority of cases the salts yield clear solutions, it is obvious that ammonolysis does not occur to an appreciable extent.

A considerable number of reactions have been studied in solvents of very low dielectric constants [49] such as benzene, toluene, etc. Reactions in these solvents often take place readily and even instantaneously. As a rule the salts dissolved are heavy metal salts of the higher organic acids such as the oleates, stearates, etc. It has been claimed that solutions of these salts are non-conductors, but the work of Cady and Lichtenwalter indicates that, while the order of conductance of solutions of salts of organic acids in benzene is low compared with that of ordinary solutions of electrolytes, nevertheless, benzene solutions conduct far more readily than does the pure solvent. In the case of a metathetic reaction with hydrochloric acid, the conductance was found to rise largely before precipitation, due, presumably, to the relatively greater conductance of the more concentrated supersaturated solution. That solutions of salts in such solvents as benzene are sufficiently ionized to exert a marked influence on the conductance is not to be doubted.

Metathetic reactions take place readily in solutions in solvents of low dielectric constants such as benzene, but, apparently, these reactions are not always instantaneous.[50] This result may in part be due to the

[49] Kahlenberg, *J. Phys. Chem.* 6, 1 (1902); Sammis, *ibid.*, *10*, 593 (1906); Gates, *ibid.*, *15*, 97 (1911); Cady and Lichtenwalter, *J. Am. Chem. Soc.* *35*, 1434 (1913); Cady and Baldwin, *ibid.*, *43*, 646 (1921).

[50] Cady and Lichtenwalter, *loc. cit.*

formation of supersaturated solutions. Reactions between silver perchlorate and hydrochloric acid, mercuric chloride and trimethyltin chloride take place instantaneously in benzene.[51] Small amounts of water greatly influence the conductance of solutions of this type.

While these results are in good agreement with the ionic hypothesis, it cannot be said that reactions cannot take place between the unionized molecules. For example, methyl iodide precipitates silver iodide in solutions of silver perchlorate in benzene. If reactions of this type are ionic, we must modify, somewhat, our notions relative to the nature of organic compounds. Yet not a few facts are in excellent agreement with such a view.

Reactions of the electrolytic type, in which one metal is substituted by another more electropositive metal, have also been studied in solvents of low dielectric constants.[52] Such reactions often take place readily. It appears not unlikely that they are in fact electrolytic. The properties of solutions of substances of the electrolytic type in solvents of low dielectric constant have received all too little attention. The data so far are too fragmentary to warrant drawing conclusions of a general nature, but it is not to be doubted that the study of such systems will lead to important results. Electrolytic phenomena are not confined to solvents of high dielectric constant. Evidence is constantly accumulating which supports the view that all fluid media possess, in some degree, the power of forming electrolytic solutions under suitable conditions.

9. *Factors Influencing Ionization.* a. *The Ionizing Power of Solvents in Relation to Their Constitution.* Since, as we have seen, the ionizing power of a solvent is largely determined by its dielectric constant, it follows that, in seeking to determine possible relations between the constitution of a substance and its ionizing power, we should seek for relations between the dielectric constant and the constitution of the substance in question. Water, hydrocyanic acid and formamide have the highest dielectric constants of substances so far investigated.

The nature of the relation between the dielectric constant and the constitution of liquid media is not clear. There is, however, an obvious relation between the dielectric constant of the hydrogen derivatives of the elements and their position in the periodic system. The hydrogen derivatives of the first members of the various groups invariably exhibit a dielectric constant much greater than that of the following members. Similarly, the dielectric constant of the hydrogen derivatives of elements

[51] Observations by Messrs. Callis and Greer in the Author's Laboratory.
[52] Gates, *loc. cit.*

in a given series increases with the order of the group. Thus, water has a dielectric constant of approximately 80 and is an excellent ionizing agent, while hydrogen sulphide has a dielectric constant of 10 and is a relatively poor ionizing agent. Ammonia at its boiling point has a dielectric constant of 22 and is a moderately good ionizing agent. In the seventh group, hydriodic acid has a dielectric constant of 2.9, hydrobromic acid of 6.3, and hydrochloric acid of 9.5. As we approach the derivatives of the upper members of this group, their dielectric constant and their ionizing power increase. The dielectric constant of hydrogen fluoride is not known but it is known to be an excellent ionizing agent. Moissan, for example, prepared fluorine by the electrolysis of fluorides in liquid hydrogen fluoride. It seems not improbable that the dielectric constant of hydrofluoric acid is greater than that of water. At any rate, in passing from ammonia to water, the dielectric constant increases from 22 to 80, and it is, therefore, not improbable that the dielectric constant of hydrogen fluoride is higher than that of water. The dielectric constant of many organic and inorganic substances containing oxygen, nitrogen, chlorine and sulphur is relatively high. Such substances in the liquid state possess the power of dissolving salts and of forming conducting solutions with them. It is unnecessary to give here a detailed list of these substances.

With increasing temperature, the dielectric constant of all substances decreases. The dielectric constants of a number of substances have been measured through the critical point.[53] These include sulphur dioxide, ether, ethylchloride, and hydrogen sulphide. For these substances the dielectric constant just beyond the critical point is 2.1, 1.52, 4.68 and 2.7 respectively. A striking result, here, is the relatively high value of the dielectric constant of ethylchloride at the critical point relative to its value at lower temperatures. Thus at 59° its value is 6.29, which decreases to the value given above at 186°. Evidently the variation of the dielectric constant with the temperature depends largely upon the nature of the solvent. Corresponding to the low value of the dielectric constant of sulphur dioxide, the conductance of solutions of electrolytes in this solvent falls to very low values. The same is true of ammonia solutions, although in this solvent the conductance above the critical point has a readily measurable value. The conductance of typical salts in ethylchloride has not been measured, but that of mercuric chloride solutions, whose ionization is usually relatively low, is greater than that of solutions of typical electrolytes in sulphur dioxide under corresponding conditions. Judging by the conductance of solutions

[53] Eversheim, *Ann. d. Phys.* 8, 539 (1902); *ibid.*, 13, 492 (1904).

in the critical regions, solvents which have a dielectric constant greater than 26 at ordinary temperatures have fairly high dielectric constants in the critical region; and, probably, the higher the dielectric constant of solvents of this type, the greater the dielectric constant in the critical region. In all likelihood, the dielectric constant of water in the critical region is fairly high. Unfortunately, there are very few data available on the relation between the dielectric constant and the variables which determine the condition of the solvent.

Among solvents of high dielectric constant, only solutions in water have been measured with any considerable degree of precision. The conductance of solutions in hydrocyanic acid indicates that the behavior of solutions of electrolytes in this solvent is similar to that in aqueous solutions, but available data are not sufficiently accurate to make it possible to determine the precise form of the conductance curve. Further data on the properties of solutions in solvents of high dielectric constant are much needed.

b. *The Relation between the Ionization Process and the Constitution of the Electrolyte.* While the ionization of an electrolyte is, in the first place, largely dependent on the dielectric constant of the solvent medium, the strongest typical electrolytes are probably ionized in all solvents, provided they are sufficiently soluble, but in solvents of very low dielectric constant ionization is appreciable only at high concentrations. The typical inorganic salts are not, as a rule, sufficiently soluble in solvents of low dielectric constant to yield solutions which conduct the current readily. However, salts of various organic bases, such as the substituted ammonium salts[54] are soluble in solvents of low dielectric constant and conduct the current.

The dielectric constant is only one of the factors governing the ionization process. For ionization is largely dependent upon the nature of the second component. For certain substances, which we ordinarily class as the typical salts, the dielectric constant of the solvent medium is largely determinative of the ionization, but even here we find that in non-aqueous solvents the ionization may vary greatly for salts whose ionization values are practically identical in water. This is true of solutions in ammonia and still more so of solutions in acetone. In these solvents, the characteristic properties of the electrolyte persist even down to the lowest concentrations for which measurements exist and these concentrations are much lower than those in aqueous solutions. No theory of electrolytic solutions can be looked upon as adequate which does not render an account of this very common property of these solutions.

[54] Walden, *Bull. Acad. Imp. des Sci.*, p. 907, No. 16 (1913), VI series.

In general, compounds between strongly electronegative and strongly electropositive constituents are electrolytes both in solution and in the fused state. This includes not only salts of strong acids and bases but also salts of weaker acids and bases. Thus, the ammonium salts are excellent conductors both in solution and in the fused state. The same is true of salts of organic bases. Here, however, we find a few marked exceptions. Thus, the trimethylin halides, $(CH_3)_3SnX$ are normally ionized in aqueous solution, but are ionized much less than other typical salts in alcohol and still less in acetone. In nitrobenzene and benzonitrile these salts are not ionized at all, although these solvents have dielectric constants higher than that of alcohol. Finally, these salts are not appreciably ionized in the liquid state.[55] It is evident that we have here an extreme case of individuality in an electrolytic substance.

In many cases, the electrolytic properties of a solution are due to interaction between the solvent and the solute whereby an electrolyte is produced. Thus, the acids are electrolytes in solution but in the pure state they exhibit a very low conductance. Indeed, the acids are electrolytes only in what may be termed basic solvents; that is, solvents capable of forming salts or salt-like substances on addition to an acid. Ammonia and ammonium salts are typical examples of a solvent and a salt of this type. Solutions of the acids in water and the alcohols probably depend for their electrolytic properties on the formation of similar complexes between the acid and the solvent.[56] When acids are dissolved in non-basic solvents, such as sulphur dioxide or nitrobenzol, the resulting solutions exhibit a very low conductance, provided the solvent is quite dry. Doubtless, similar considerations hold for solutions of acidic substances, such as the acid amides in ammonia.[57] So, also, solutions of many organic oxygen and nitrogen compounds in the liquid halogen acids owe their electrolytic properties to the formation of a more or less stable complex between the dissolved substance and the acid solvent. The inorganic bases, while intimately related to the acids from the standpoint of their constitution in aqueous solution, are otherwise to be classed as salts. The properties which they exhibit are throughout characteristic of salts.

In general, compounds, in which distinctly electropositive and electronegative constituents are not present, are not electrolytes; or, at any rate, in a fused state they are relatively poor conductors of the electric

[55] Observations by Mr. C. C. Callis in the Author's Laboratory.

[56] Kendall and Gross, *J. Am. Chem. Soc.* *43*, 1426 (1921), have investigated the conductance of mixtures of acids with esters, ketones and other acids and have found unmistakable signs of the formation of compounds.

[57] The acid amides do not conduct in water probably owing to the fact that these substances act as very weak bases in water, whose acidic properties are much greater than those of ammonia.

current and in solution their conductance is low. Nevertheless, solutions of non-polar substances may exhibit marked electrolytic properties. So, for example, solutions of iodine bromide, iodine trichloride, iodine, phosphorus trichloride, phosphorus pentabromide, etc., conduct the current to a measurable extent in sulphur dioxide, arsenic trichloride, sulfuryl chloride, nitrobenzene,[58] etc. So, also, for example, solutions of iodine in bromine conduct the current. Walden has suggested that in these solutions one electronegative atom functions as anion and another as cation. For example, he assumes that a reaction of the type:

$$I_2 = I^+ + I^-,$$

takes place when iodine is dissolved in sulphur dioxide. The investigations of Bruner and Galecki [59] and Bruner and Bekier [60] have shown that, in sulphur dioxide and nitrobenzol, the halogens and their compounds are not constituents of the positive ions. At any rate, on electrolyzing such solutions, the negative element may be concentrated at the anode. The nature of the cation in these solutions is uncertain, but there appears to be little doubt that the electronegative constituent is associated with the anion. Apparently, the electrolytic properties of these solutions are due to the formation of a complex between the strongly electronegative element or compound and the solvent, in which, presumably, the solvent molecule, in part at least, functions as cation.

So far as the electrolytic properties of their compounds are concerned, strongly electronegative elements or groups of elements may not function as cations, although it is possible that in certain cases they may be associated with the cation in the form of a complex ion, as is the case, for example, with iodine in the intermediate ion of cadmium iodide in aqueous solution. On the other hand, as we have already seen, metals, which normally are electropositively charged in their compounds with more electronegative elements, may, under certain conditions, function as anions. For example, sodium and lead in ammonia react to form a solution in which the two elements are present in the ratio of 2.25 atoms of lead to one atom of sodium, when metallic lead is present in excess.[61] On electrolysis of these solutions, lead is precipitated on the anode. The properties of these complex anions have already been discussed.

[58] Walden, *Ztschr. f. phys. Chem.* *43*, 385 (1903).
[59] Bruner and Galecki, *Ztschr. f. phys. Chem.* *84*, 513 (1913).
[60] Bruner and Bekier, *ibid.*, *84*, 570 (1913).
[61] Kraus, *J. Am. Chem. Soc.* *29*, 1557 (1907); Smyth, *ibid.*, *39*, 1299 (1917).

Chapter XII.

Theories Relating to Electrolytic Solutions.

1. *Outline of the Problem Presented by Solutions of Electrolytes.* The problem of electrolytic conduction presents a twofold aspect depending upon the point of view from which it is approached. On the one hand, we are concerned with certain well defined equilibria, the laws governing which it is attempted to discover; on the other, we are concerned with the mechanism of the process whereby the conduction of the electric current is effected. In the first case the principles governing equilibria in mixtures are applied, supported by various auxiliary assumptions which are necessary if an explicit solution of the problem is to be reached. These assumptions usually involve the equation of state of the system, the precise form of which is not known. A general solution, therefore, cannot be reached by this method. In order to disclose the mechanism of the conduction process, a knowledge of the forces acting between the conducting particles and their surroundings is required. Since the laws governing these forces are not known, a solution is not possible by this method. Furthermore, if a force function is assumed, a solution can be reached only by the application of statistical methods and these methods have not been developed to a point where their application to electrolytic systems can be made with any degree of certainty. In either case, therefore, a point is soon reached where the results obtained are little more than conjectures. The probable correctness of the results obtained may be checked by comparison with experiment. In practice it is often found that, while the results of one method agree fairly well among themselves, they disagree with those obtained by the alternative method. That the two methods must lead to results which are in mutual agreement is not to be doubted. Lack of agreement indicates that various assumptions made are not permissible.

It may be expected that a solution of the problem will first be reached for mixtures where the concentration of the electrolytic component is so low that various effects, due to the interaction of the ions and other molecular species present, become negligible. Here, however, the difficulty arises that experimental data become very uncertain. Nevertheless, ap-

preciable progress has been made in this direction. In dilute solutions of weak electrolytes, the ionic theory has met with marked success and, while it may be expected that here, too, the theory will have to be materially modified when a final solution of the problem has been reached, the mutual consistency of the results obtained indicates that a considerable measure of truth underlies the ionic theory as formulated. This important fact should not be lost sight of in developing a more general theory of electrolytic solutions.

The inapplicability of the law of mass action in its simple form to relatively dilute solutions of strong electrolytes has led to many controversies relative to the nature of these solutions. On the one hand, it has been suggested that such solutions are completely ionized at all concentrations;[1] and, on the other, that they are not ionized at all.[2] Still other theories attempt to relate these solutions with colloidal systems.[3] The proposed theories may be grouped into three classes: (1) theories which are derived by combining with thermodynamic principles auxiliary assumptions, which, in part at least, are of an empirical nature; (2) theories in which the interionic forces due to the charges are taken into account; and (3) theories of a miscellaneous nature which as a rule are of a qualitative character.

2. *Electrolytic Solutions from the Thermodynamic Point of View.* a. *Scope of the Thermodynamic Method.* If equilibria exist in solutions of electrolytes, as we have reason to believe, then such solutions must be subject to the thermodynamic principles governing equilibria. That equilibria, in fact, exist in electrolytic systems is not to be doubted, since in no other class of systems do reactions proceed so rapidly to a definite condition. In most instances, it is not possible to measure the speed with which reaction takes place in these solutions. The first assumption which arises in the detailed application of the principles of thermodynamics to equilibria in solutions of electrolytes is that of the precise nature of the reaction involved. It is obvious that, before equilibria of the electrolytic type can be treated comprehensively, the nature of the reactions involved must be definitely established. All considerations in which these reactions are involved are necessarily subject to uncertainty, since it has not been found possible to establish, definitely, whether or not un-ionized molecules, as well as ions, exist in electrolytic solutions. The nature of the reaction being assumed, the thermodynamic treatment of electrolytic solutions is comparatively simple, so far as the thermodynamic considerations themselves are concerned. When, how-

[1] Ghosh, *Trans. Chem. Soc.* *113*, 449 (1918).
[2] Snethlage, *Ztschr. f. phys. Chem.* *90*, 1 (1915).
[3] Georgievics, *Ztschr. f. phys. Chem.* *90*, 341 (1915).

ever, the concentrations of the various constituents present in the solution are such that the laws of ideal systems are no longer applicable within the limits of experimental error, a general solution of the problem is, at the present time, not possible. In other words, the general solution of the problem involves a knowledge of the equation of state of the system. According to the equilibrium principle of Gibbs, a system will be in stable equilibrium when the entropy is a maximum. For many purposes it is more convenient to introduce derived functions such as the Gibbsian functions ψ and ζ in place of the entropy. For a mixture of any number of components in a system, not subject to reaction, the free energy is given by the equation:

(98)
$$\psi = \int_v pdv + RT\ [(1\text{-}x\text{-}y\text{-}z\text{-}\cdots)\ \log\ (1\text{-}x\text{-}y\text{-}z\text{-}\cdots) + x \log x + y \log y + z \log z + \cdots\ ] + F(xyz\,..\,T),$$

where x, y, z, etc., represent the amounts of the various constituents present per gram mol of the mixture. The term $F(xyz..T)$ is, in general, a determinable function of temperature and a linear function of xyz... The term $\int_v pdv$ is a function of the concentrations xyz.., and represents the work done in bringing the system from a condition in which the laws of an ideal system are obeyed to the condition in which the system obeys any given equation of state.[4] It is obvious that the condition for equilibrium, $d\psi = 0$, may at once be applied if the equation of state is known, while, if the equation of state is not known, the problem is necessarily insoluble, since it is not possible to evaluate the integral in question. When reaction takes place between various constituents present in the mixture, the condition for equilibrium leads to the equation:

(99)
$$\Sigma M = 0,$$

where

(100)
$$M = m\mu.$$

Here m is the molecular weight of the constituent and μ is the thermodynamic potential defined according to Gibbs.[5] The molecular potential M, of a constituent, is given by an equation of the form:

(101)
$$M = RT \log x + F(vT\ xyz..)$$

where $F(vT\ xyz..)$ is a function of the composition of the system, as well as of volume and temperature, except when the equation of state of

[4] van der Waals-Kohnstamm, "Lehrbuch der Thermodynamik," Vol. 2 (1912).
[5] Gibbs, Scientific Papers, Vol. 1, pp. 92 *et seq.* (1912).

the system fulfills the condition $pv = RT$, in which case the only manner in which the concentration is involved in the expression for the thermodynamic potential is in the logarithmic term of the above equation. In order to evaluate the term $F(vT\,xyz..)$ it is necessary to know the equation of state of the system, since the value of M as given by the equation:

$$(102) \qquad M = \psi - v\left(\frac{\delta\psi}{\delta v}\right)_{xT} - x\left(\frac{\delta\psi}{\delta x}\right)_{vT} - \cdots,$$

obviously involves the term $\int_v pdv$, which cannot be evaluated without a knowledge of the equation of state. The equations of state for mixtures of ordinary liquids are comparatively complex, and a general solution of the problem has not been effected, even for liquids of simple type; while, in the case of mixtures of substances whose equations of state are comparatively complex, even an approximate solution has been little more than attempted. This subject has been treated in detail by van der Waals.[6]

b. *Jahn's Theory of Electrolytic Solutions.* Nernst[7] and Jahn[8] attempted to solve the problem of solutions of strong electrolytes by introducing various correction terms. Since the true equation of state for mixtures containing electrolytes is not known, even approximately, it is obvious that these theories necessarily involve assumptions of an arbitrary nature. These assumptions must contain within them the equivalent of an equation of state. In how far these assumptions are allowable may be ascertained by comparing the consequences of these theories with the experimental facts. Jahn set up the conditions for equilibrium, employing as a criterion for equilibrium, the variation of Planck's function:

$$\varphi = -\frac{\zeta}{T}.$$

It is on the whole immaterial what function is employed as criterion for equilibrium, provided, always, that it fulfills the conditions of a characteristic function.[9] These functions involve the energy of the system and, in order that the condition for equilibrium may be solved, it is necessary to have an expression for the energy of the system in terms of its composition. In the case of ideal systems, Dalton's law may be assumed to hold, in which case the energy of a mixture of substances is equal to the sum of the energies of its constituents. Jahn assumed an equation for

[6] van der Waals-Kohnstamm, *loc. cit.*
[7] Nernst, *Ztschr. f. phys. Chem.* *38*, 487 (1901).
[8] Jahn, *Ztschr. f. phys. Chem.* *41*, 257 (1902).
[9] Gibbs, Scientific Papers *1*, pp. 85 *et seq.* (1906).

the energy containing cross terms due to forces acting between the different molecular species present in the mixture. This assumption, which is necessary for a solution of the problem by this method, is obviously an arbitrary one. Proceeding in this way Jahn obtains, for a system of electrolytes in equilibrium, the equation:

$$\log \frac{(C_i)^2}{C_u} = (\alpha + \beta\gamma)C + \log K_0, \tag{103}$$

where α and β are constants. The constancy of the functions α and β however, depends upon the original assumption made with regard to the manner in which the energy of the system is dependent upon its composition, and, if a different assumption had been made, it would have led to a corresponding variation in the resulting equation. Methods of this kind are correct enough thermodynamically, but, in order that they may lead to results which may be tested experimentally, an assumption must be made, and this assumption is, in general, arbitrary in its nature. In this sense, therefore, the results of these methods are to be looked upon as being purely empirical in character, unless evidence of an *a priori* nature can be adduced in favor of the assumptions made. In all cases, the correctness of the assumptions may be tested by comparing the resulting equations with the experimental values. Taking the equation of Jahn, it is easy to make a comparison with experiment.

This equation obviously involves four constants; namely, α, β and K_0, together with Λ_0, the limiting value of the equivalent conductance. The equation is a fairly complex one and it is not easy to extrapolate for the value of Λ_0 on the basis of this equation, but it may safely be assumed that, in the case of potassium chloride, the conductance of whose solutions has been measured to 2×10^{-5} normal, the true value of Λ_0 does not differ materially from that ordinarily assumed. At higher concentrations, at any rate, a slight error in the value of Λ_0 will cause a relatively small change in the distribution of the points. Assuming the value of Λ_0, and calculating the values of the function K' at three concentrations, it is possible to evaluate the constants α, β and K_0. The values of α and β being known, the equation may be tested by plotting values of log K against those of $(\alpha + \beta\gamma)C$. This plot should yield a linear relation, but, in fact, leads to results inconsistent with the experimental values. The value of K' has a maximum in the neighborhood of 0.05 normal, after which it decreases rapidly. The equation as calculated for potassium chloride at 18° is as follows:

$$\log K' = 2.5935 + (592.8 - 498.7\gamma)C.$$

While Jahn's equation has not been tested in the case of non-aqueous solutions, it is easy to see that it cannot hold generally. For example, for $m = 1$ in Equation 11, the function K' varies practically as a linear function of the ion concentration. Such an equation will not reduce to the form of that of Jahn.

That Jahn's equation should not hold is in no wise surprising, since the assumptions underlying it are of an arbitrary nature. It is improbable that the free energy of electrolytic solutions may be determined as a function of concentration without the aid of an equation of state. In other words, the chance of finding the correct equation by mere accident would appear to be vanishingly small. The method of Nernst does not differ materially from that of Jahn and leads to a similar result.

c. *Comparison of the Thermodynamic Properties of Electrolytes. Inconsistencies in the Older Ionic Theory.* While the application of thermodynamic principles yields no information relative to the mechanism involved in electrolytic solutions, these principles when combined with other hypotheses lead to consequences which admit of verification.

The bearing of thermodynamics on the theory of electrolytic solutions was long neglected and has often been misinterpreted. So, for example, the correspondence between the ionization values as derived from conductance and from osmotic measurements was looked upon as lending support to the older ionic theory. As Nernst[10] pointed out, this apparent confirmation of the ionic theory constitutes, in fact, one of the chief obstacles in the path of its acceptance.

Insofar as electrolytic solutions constitute systems in which equilibria prevail, thermodynamic principles are applicable. It is evident, however, that the laws of dilute solutions are not applicable to these systems at ordinary concentrations. Aside from a few very general relations, the application of thermodynamic principles alone can furnish us very little information relative to the nature of these solutions. The general problem is to express the potentials of the various constituents in terms of the independent variables of the system; that is, of the concentrations of the various substances present. Since statistical and other methods have not been developed to a point where they enable us to determine the equation of state of these systems, the problem at the present time can be attacked only by experimental methods. Fortunately, the potentials of electrolytes in solution may be determined readily and with a relatively high degree of precision. The values of the potentials as thus determined may be treated by graphical or other empirical methods; and, while the theoretical relation between the potentials and the concentra-

[10] Nernst, *Ztschr. f. phys. Chem.* *38*, 493 (1901); Jahn, *ibid.*, *38*, 125 (1901).

tions of the constituent electrolytes remains undisclosed, the form of the function may be determined. At the same time, the values of the potentials of different electrolytes may be compared and relationships brought to light which are of practical importance, even though their theoretical significance may not be apparent. Our knowledge of electrolytes from this point of view is restricted to aqueous solutions. In view of the fact that many properties of electrolytic solutions are greatly modified in solvents of lower dielectric constant, and since the similarity in the behavior of dilute aqueous solutions of different electrolytes is not often found in other solvents, any generalization of the results obtained in aqueous solutions must be made with caution.

The Thermodynamic Method. The significance of the results obtained from an examination of the thermodynamic properties of electrolytic solutions will be better understood if treated without reference to detailed methods. Let us assume that we have a solution in which the following reaction takes place:

$$n_1A_1 + n_2A_2 + \cdots = n_1'A_1' + n_2'A_2' + \cdots$$

The condition for equilibrium in such a solution is:

$$\Sigma nM = \Sigma n'M'. \tag{104}$$

The potential sum for the constituents on either side of the reaction equation may be expressed by a function of the form:

$$\Sigma nM = F(C_1, C_2, \ldots C_1', C_2', \ldots), \tag{105}$$

where $C_1, C_2, \ldots C_1', C_2', \ldots$ are independent variables. If any of these variables are not independent, a relation will evidently exist among them by means of which they may be eliminated. So long as we are dealing with a solution of a single electrolyte, the potential may obviously be expressed as a function of the concentrations of the ions and the un-ionized fraction; that is, we have:

$$\Sigma nM = F(C^+, C^-, C_u). \tag{106}$$

Since a relation exists between the concentrations C^+, C^- and C_u, it is obvious that one of these variables is not independent. Since, in general, it is not possible to determine the concentration of the ions and of the un-ionized fraction in a solution of an electrolyte, the total concentration of the salt may equally well be employed for practical purposes, in which case:

$$\Sigma nM = F(C_s). \tag{107}$$

If the value of the potential sum ΣnM may be experimentally determined at different concentrations, the form of the function $F(C_s)$ is empirically known. If the experimental values of ΣnM are correct, then the values of $F(C_s)$, as determined by different methods, must necessarily be in agreement. This result has been verified by Lewis and Randall,[10a] as we shall see below. When mixtures of electrolytes are employed, the expression for the potential obviously becomes a function of a greater number of variables. In the case of a salt in the presence of another salt with a common ion, the potential becomes a function of two variables; and in that of a salt without a common ion, of three variables. We should not expect, therefore, that the values obtained for the potential sum in mixtures could be directly compared with those obtained for the same electrolytes in a pure solvent. The methods which have been adopted by investigators in this field, however, have consisted essentially in expressing the potential of an electrolyte in a mixture as a function of a single variable. This method consists in introducing a variable defined by an equation of the form:

$$C_m = F(C_1, C_2, \ldots). \tag{108}$$

This function is given such a form that the value derived for the potential sum in the mixture, on introducing C_m as variable, corresponds with that of a solution of the pure substance when the same variable is introduced. If such a function exists, then we are led to conclude that the potential sum for a given electrolyte in solution is dependent, not upon the concentrations of the various substances involved, but upon some other single parameter.

The potential of an electrolyte as a function of its concentration may be determined directly by means of the electromotive force of concentration cells. More indirectly, the potential may be obtained from the vapor pressures of these solutions and from other related properties, such as the freezing point, boiling point, etc. If the experimental determinations are correct, the values of the potentials derived from the measurement of these different properties must necessarily be in agreement with one another.

Lewis and Randall [11] have compared the available experimental data for aqueous solutions in this way, and have found them to be in excellent agreement. This implies the correctness of the methods employed in calculating the various thermodynamic quantities, as well as the accuracy

[10a] Lewis and Randall, *J. Am. Chem. Soc.* *43*, 1112 (1921).
[11] *Idem, loc. cit.*

of the experimental methods, by means of which the data were secured. The practical application of thermodynamic principles to electrolytic solutions is largely due to G. N. Lewis.[12] In recent years numerous other writers have occupied themselves with this subject.[13] The writers on this subject have commonly employed the activity function of Lewis,[14] which is defined by the equation:

$$M = RT \log a + i_0, \tag{109}$$

where a is the activity and i_0 is a function independent of the concentration of the constituent in question. The ratio of the activity of a substance to its concentration is termed its activity coefficient and is thus defined by the equation:

$$\alpha = \frac{a}{C}. \tag{110}$$

In a solution of an electrolyte we have an equilibrium of the type:

$$n^+A_1^+ + n^-A_2^- = A',$$

where A' represents a molecule of substance which dissociates into n^+ positively charged ions A_1^+ and n^- negatively charged ions A_2^-. The number of charges on the ions is not indicated. Introducing the values of M from Equation 109 in Equation 104 we may at once derive the expression:

$$\log \frac{a^{+n^+} a^{-n^-}}{a_u} = K, \tag{111}$$

where a^+, a^-, and a_u denote the activities of the positive and negative ions and the un-ionized molecules, respectively, and K is a function independent of concentration. For the change in the potential of the electrolyte between any two concentrations of the system, we have the equations:

$$(\Sigma n'M')_b - (\Sigma n'M')_a = RT \log \frac{a_{u_b}}{a_{u_a}}, \tag{112}$$

$$(\Sigma nM)_b - (\Sigma nM)_a = RT \log \frac{a^+{}_b^{n^+} \, a^-{}_b^{n^-}}{a^+{}_a^{n^+} \, a^-{}_a^{n^-}}. \tag{113}$$

[12] Lewis, *J. Am. Chem. Soc.* *34*, 1631 (1912).

[13] Brönsted, *J. Am. Chem. Soc.* *42*, 761 (1920); Bjerrum, *Ztschr. f. Elektrochemie* *24*, 321 (1918); *Ztschr. f. Anorg. Chem.* *169*, 275 (1920); Harned, *J. Am. Chem. Soc.* *42*, 1808 (1920).

[14] Lewis, *Proc. Am. Acad.* *43*, 259 (1907); *Ztschr. f. phys. Chem.* *61*, 129 (1907); *ibid.*, *70*, 212 (1909).

From Equation 112, the ratio of the activities of the un-ionized molecules for any two conditions of the solution may be determined if the potential change is known. Similarly, the ratio of the activity products of the ions may be determined from Equation 113. The actual value of the activity product is not in general determinable. At low concentrations, however, as is apparent from Equation 109, the activity a approaches a value equal to that of the concentration C. If the potential can be determined at sufficiently low concentrations, that is, in solutions sufficiently dilute so that the laws of dilute solutions become applicable, the true values of the activity products may be determined. In systems in which a reaction takes place among the constituents the concentrations C are not usually determinable, so that the value of the true activity coefficients α remains undetermined. For practical purposes, therefore, a new activity coefficient has been introduced, defined by the equation:

$$\alpha_s = \frac{a}{C_s}, \tag{114}$$

where C_s is the total concentration of the electrolyte. Further, instead of employing the values of the product of the activity coefficients, some function of the product of these coefficients is employed which makes the resulting coefficient more nearly comparable with that of a solution of a single molecular species. For electrolytes, Lewis and Randall have introduced a coefficient α_r, defined by the equation:

$$\alpha_r = \frac{(a_+^{n^+} a_-^{n^-})^{\frac{1}{n^+ + n^-}}}{(C_s{}_+^{n^+} C_s{}_-^{n^-})^{\frac{1}{n^+ + n^-}}} = \frac{a_r}{C_r}. \tag{115}$$

where a_r and C_r may be called the reduced activities and the reduced concentrations of the ions.[15] In a solution of a binary electrolyte:

[15] The nature of the various coefficients may be further elucidated by writing the equations for the potential sum in somewhat more explicit form. We have:

$$\Sigma nM = RT\Sigma n \log C + \Sigma ni_0 + \Sigma nJ, \tag{117}$$

where

$$\Sigma nJ = RT\,\Sigma n \log \frac{a}{C}.$$

It is evident that this equation is not capable of being employed practically as an interpolation function, since C is not determinable. If, now, C is replaced by C_s, the total salt concentration of the electrolyte in solution in pure water,

$$\Sigma nM = RT\,\Sigma n \log C_s + \Sigma ni_0 + \Sigma nJ_s \tag{118}$$

If the values of ΣnM are known for different values of C, then the variation in the function ΣnJ_s over the concentrations in question is likewise known. In Equation 117, ΣnJ measures the change in the value of the potential of a substance in a real system above that in an ideal system at the same concentration. When the reduced concentration

(116) $$\alpha_r = \alpha_s = \left[\frac{a^+a^-}{C_s^2}\right]^{1/2}.$$

Numerical Values. In comparing the thermodynamic behavior of different electrolytes, Lewis and Randall have compared the values of the reduced activity coefficients α_r at corresponding concentrations. In Table CXXX are given values of the activity coefficients of different electrolytes at a number of concentrations. These values have been

TABLE CXXX.

ACTIVITY COEFFICIENTS OF VERY DILUTE AQUEOUS SOLUTIONS AT DIFFERENT CONCENTRATIONS.

	0.01	0.005	0.002	0.001	0.0005	0.0002	0.0001
KCl, NaCl ...	0.922	0.946	0.967	0.977	0.984	0.990	0.993
KNO_3	0.916	0.943	0.965	0.976	0.984	0.990	0.994
KIO_3, $NaIO_3$.	0.882	0.915	0.946	0.961	0.972	0.982	0.988
K_2SO_4	0.687	0.749	0.814	0.853	0.885	0.917	0.935
H_2SO_4	0.617	0.696	0.782	0.831	0.871	0.910	0.932
$BaCl_2$	0.716	0.771	0.830	0.865	0.894	0.923	0.939
$CoCl_2$	0.731	0.784	0.840	0.873	0.900	0.927	0.943
$MeSO_4$	0.40(4)	0.50	0.61	0.69	0.75	0.81	0.85
$K_3Fe(CN)_6$ ..	0.571	0.657	0.752	0.808	0.853	0.897	0.922
$La(NO_3)_3$	0.571	0.657	0.752	0.808	0.853	0.897	0.922

derived from freezing point measurements and agree well with those derived by other methods. In Figure 59, the continuous curve represents the values of the activity coefficients of sodium chloride at different concentrations as derived from freezing point determinations, while the points indicated by circles represent values of the coefficients as derived

C_s is introduced, ΣnJ_s measures this change of potential, together with the variation due to the substitution of C_s for C. If we write:

$$\Sigma nJ_s = RT\,\Sigma n \log a_s$$

and introduce this function into the equation for the activity, we have:

$$RT\,\Sigma n \log a = RT\,\Sigma n \log C_s + RT\,\Sigma n \log a_s,$$

whence:

$$\Sigma n \log a_s = \Sigma n \log \frac{a}{C_s}.$$

This equation defines the stoichiometric activity coefficient of Brönsted. If salts were completely ionized, the coefficient $a_s = a/C_s$ would be a measure of the true activity coefficient. Since potential measurements yield values of the activity products only, an assumption is necessary if the activity coefficient is to be defined by means of an equation of the form:

$$a_r = F\left(\frac{a^+a^-}{C_s^2}\right).$$

In mixtures of any number of electrolytes the definition of the total salt concentration also becomes uncertain and a further assumption of an arbitrary nature is involved in defining the activity coefficients.

from electromotive force determinations.[15a] It is evident that the activity coefficients, as determined by the two methods, are in remarkably good agreement. This indicates the correctness of the methods employed in the calculations, as well as the accuracy of the experimental data. Similar calculations have been made for aqueous solutions of

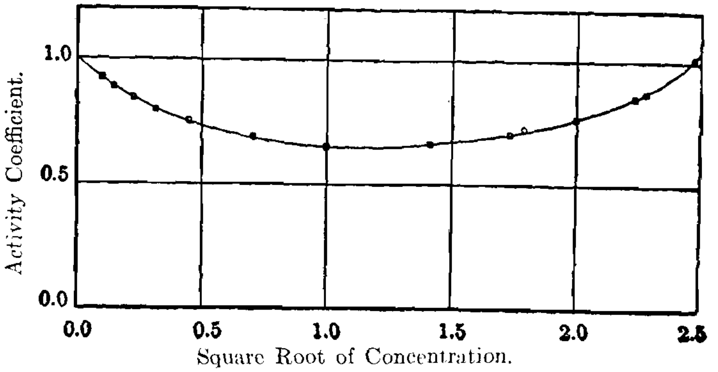

Fig. 59. *Activity Coefficients of Sodium Chloride Solutions as a Function of Concentration.*

sulphuric acid by the freezing point, electromotive force, and vapor pressure methods. Here, again, the results of the different methods have been found to be in excellent agreement. In Table CXXXI are given values of the activity coefficients of typical electrolytes at higher concentrations.

TABLE CXXXI.

Activity Coefficients of Typical Electrolytes.

$C =$	0.01	0.02	0.05	0.1	0.2	0.5	1	3
HCl(25°)	0.924	0.894	0.860	0.814	0.783	0.762	0.823	1.35
LiCl(25°)	0.922	0.892	0.843	0.804	0.774	0.754	0.776	1.20
NaCl(25°) ...	0.922	0.892	0.842	0.798	0.752	0.689	0.650	0.704
KCl(25°)	0.922	0.892	0.840	0.794	0.749	0.682	0.634	..
KOH(25°) ...	0.92	0.89	0.84	0.80	0.75	0.73	0.75	..
KNO_3	0.916	0.878	0.806	0.732	..	..	..	..
$AgNO_3$	0.902	0.857	0.783	0.723	0.655	0.526	0.396	..
KIO_3, $NaIO_3$ ..	0.882	0.840	0.765	0.692	..	..	..	..
$BaCl_2$	0.716	0.655	0.568	0.501	..	..	..	..
$CdCl_2$(25°) ...	0.532	0.44	0.30	0.219	..	..	..	..
K_2SO_4	0.687	0.614	0.505	0.421	..	..	..	..
H_2SO_4(25°) ...	0.617	0.519	0.397	0.313	0.244	0.178	0.150	1.70
$La(NO_3)_3$	0.571	0.491	0.391	0.326	0.271	..	..	..
$MgSO_4$	0.404	0.321	0.225	0.166	0.119	..	..	..
$CdSO_4$	0.404	0.324	0.220	0.160	..	..	..	..
$CuSO_4$	0.404	0.320	0.216	0.158	0.110	0.067	..	..

[15a] Allmand and Polack, *Jour. Chem. Soc.* **115**, 1020 (1919).

As may be seen by reference to Table CXXX, the activity coefficients of electrolytes of the same type do not differ greatly at low concentrations. The activity coefficient increases as the concentration decreases at low concentrations. In solutions of strong acids and bases and of the alkali metal chlorides, the activity coefficients pass through a minimum at high concentrations. This, however, does not appear to be a general property of electrolytes, since silver nitrate does not exhibit a minimum up to concentrations of 5 molal. The higher the type of salt, the more rapidly does the activity coefficient decrease with increasing concentration. While, as a rule, salts of the same type exhibit the same values of the activity coefficients, a number of exceptions occur, such as cadmium chloride, whose activity coefficient at 0.1 M is 0.219, while that of barium chloride at the same concentration is 0.50. Aqueous solutions of electrolytes are remarkable for the uniformity of the phenomena presented. At low concentrations, many properties of these solutions differ only inappreciably for different electrolytes of the same type. The same relation is found in the case of the activity coefficients. At higher concentrations, however, different electrolytes exhibit considerable variations.

At low concentrations, the values of the reduced activity coefficients $\frac{a}{C_S}$ approach those of the ionization coefficient $\gamma = \frac{\Lambda}{\Lambda_0}$. The significance of this result is uncertain, since, even at the lowest concentrations, aqueous solutions of strong electrolytes do not conform to the requirements of the law of mass action.

A comparison of the activity coefficients of solutions of pure electrolytes with those of mixtures cannot be effected without some further assumption. *A priori*, we should not expect the activity coefficient of a given salt in a mixture of electrolytes to correspond closely with that in a solution of the pure substance. From Harned's measurements on the electromotive force of concentration cells with mixed electrolytes, Lewis and Randall draw the conclusion that "in any dilute solution of a mixture of strong electrolytes, of the same valence type, the activity coefficient of each electrolyte depends solely upon the total concentration." Where the mixture contains salts of different valence types, they have introduced a new concentration function defined by the equation:

$$(119) \qquad C_m = \frac{v_1^2 C_{S_1} + v_2^2 C_{S_2} + \dots v_{r2} C_{S_r}}{2},$$

where C_S is the total molal concentration of an ionic constituent in the solution and v is the number of charges which it carries. This quantity,

C_m, which is termed the ionic strength, is employed to express the activity coefficient of a salt in a mixture in terms of a single variable. From their results they conclude that "in dilute solutions the activity coefficient of a given strong electrolyte is the same in all solutions of the same ionic strength."

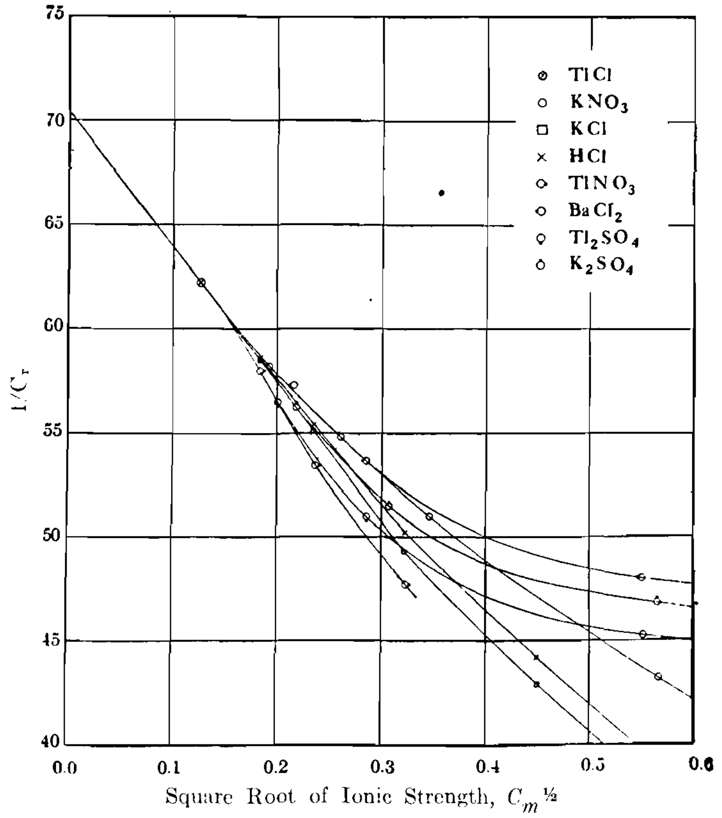

FIG. 60. Variation of $1/C_r$ for Thallous Chloride as a Function of the Ionic Strength, $C_m^{1/2}$.

In Figure 60 are represented values of the reciprocal of the mean molality of thallous chloride, defined according to Equation 115, against values of the square root of C_m, defined according to Equation 119. In Table CXXXII are given values of the activity coefficients of thallous chloride as determined from solubility experiments.

TABLE CXXXII.

ACTIVITY COEFFICIENTS OF THALLOUS CHLORIDE IN MIXTURES AT 25°.

C_m	In KNO_3	In KCl	In HCl	In $TlNO_3$
0.001	0.970	0.970	0.970	0.970
0.002	0.962	0.962	0.962	0.962
0.005	0.950	0.950	0.950	0.950
0.01	0.909	0.909	0.909	0.909
0.02	0.872	0.871	0.871	0.869
0.05	0.809	0.797	0.798	0.784
0.1	0.742	0.715	0.718	0.686
0.2	0.676	0.613	0.630	0.546

As may be seen from the figure, the curves, connecting the reciprocal of the mean reduced concentration $\frac{1}{C_r}$ with the ionic strength, diverge largely at higher concentrations. With electrolytes of the same type, such as potassium chloride and hydrochloric acid, the divergence is not large. With potassium nitrate, however, the divergence at higher concentration is marked, as is also that for the ternary electrolytes, barium chloride, thallous sulphate, and potassium sulphate. In view of the fact that these curves necessarily pass through a point corresponding to a saturated solution of pure thallous chloride, the conclusion of Lewis and Randall that the curves become coincident at lower concentrations is open to doubt, for it is conceivable that, since the curves exhibit a marked curvature at higher concentration, such curvature may be maintained in mixtures at lower concentration.

Lewis and Randall have also examined the solubility curves of higher types of salts, and have shown that, for limited concentration intervals, their principle of mixtures is able to account for the observed phenomena quite closely.

Solubility Relations According to Brönsted. Brönsted[16] has also treated the solubility relations of mixtures of electrolytes.[16a] He assumes that the van't Hoff factor i may be expressed as a function of the concentration by means of the equation: [16b]

$$(120) \qquad 2 - i = \varkappa C^{1/3},$$

[16] Brönsted, *loc. cit.*

[16a] Brönsted's theory of the solubility effects in mixtures of electrolytes is simply interpreted in terms of Bjerrum's theory of electrolytic solutions. Bjerrum assumes that electrolytes are completely ionized and that the observed effects are due to interaction between the ions. So far as the experimental foundation of Bjerrum's theory is concerned, however, it is based chiefly upon observations in mixtures of electrolytes. Naturally, Bjerrum's theory, in the case of a solution of a pure electrolyte, is in harmony with that of Milner. See Bjerrum: *D. Kgl. Danske Vidensk. Selsk. Skrifter* (7), *4*, 1 (1906); *Proc. 7th Intern. Congr. Appd. Chem.*, Sect. X (1909); *Ztschr. f. Electroch. 17*, 392 (1911); *ibid.*, *24*, 321 (1918).

[16b] Noyes and Falk, *J. Am. Chem. Soc. 32*, 1011 (1910).

where C is the molal concentration and $\varkappa$ is a constant characteristic of the salt. Combining this empirical equation with the differential thermodynamic equations and integrating, he obtains the equation:

$$\log C^+C^- = 2\varkappa C_t^{1/3} + \text{Const.,} \tag{121}$$

where C_t is the total salt concentration of the saturated solution. In the case of salts without a common ion, Brönsted assumes:

$$C^+ = C^- = C_s,$$

where C_s is the total concentration of the saturating salt. This leads to the equation:

$$\log \frac{C_s}{C_{s_0}} = \varkappa(C_t^{1/3} - C_{s_0}^{1/3}). \tag{122}$$

For the solubility of a salt in a mixture containing a salt with a common ion, Brönsted assumes:

$$C' = C_s \quad \text{and} \quad C'' = C_t,$$

where C' and C'' are the concentrations of the uncommon and the common ion respectively. This leads to the equation:

$$\log \frac{C_sC_t}{C_{s_0}^2} = 2\varkappa(C_t^{1/3} - C_{s_0}^{1/3}). \tag{123}$$

These equations express the solubility of the saturating salt in terms of the total concentration of all the salts in solution. The value of the constant $\varkappa$ depends upon the type of salt. For uni-univalent salts, $\varkappa$ = approximately 1/3; for bi-bivalent salts, 4/3; and for tri-trivalent salts, 3. Brönsted shows, in the first place, that the form of the curve is determined by the values of the constants C_{s_0} and $\varkappa$. In the presence of salts without a common ion, the solubility of the saturating salt is increased due to addition of the second electrolyte; and this increase is the greater, the greater the value of the constant $\varkappa$. Moreover, the relative increase of the solubility is the greater, the smaller the value of C_{s_0}. In the presence of salts with a common ion, the form of the solubility curve depends upon the number of charges on the ions and the number of ions resulting from the different salts. Brönsted shows that solubility curves will, in general, exhibit a minimum. In the case of uni-univalent salts, this minimum will lie at very high concentrations; for bi-bivalent salts, assuming $\varkappa = 4/3$, the minimum concentration is $0.12\,m$; and for tri-

trivalent salts, assuming $\varkappa = 3$, the minimum is at 0.01 *m*. Brönsted's equations therefore account for the solubility relations of various salts in a general way, including the minima which have been observed in the case of salts of higher type. Adjusting the value of the constant $\varkappa$ to represent the experimental values in the best possible manner, Brönsted has shown that his equations account for the observed solubilities up to 0.1 N, practically within the limits of experimental error.

According to Brönsted's equation, the activity of all salts ultimately passes through a maximum. Under these conditions, the solutions will be unstable at the maximum point and the system in these regions should separate into two liquid phases. In the case of salts of higher type, the concentration at which this phenomenon should occur lies in regions where the concentration is fairly low. Brönsted has actually been able to observe separation of a liquid phase in solutions of salts of certain trivalent ions.

The results obtained, on comparing the thermodynamic potential of electrolytes in aqueous solution, show that these values as derived by different methods are in excellent agreement. Thermodynamic principles alone are not capable of supplying information as to the nature or number of the molecular species present in electrolytic solutions. The results are naturally in agreement with the assumption that electrolytes are completely ionized and, in view of the fact that in the thermodynamic treatment we are restricted to total concentrations and not to actual concentrations, the results are most simply interpreted on the basis of this hypothesis. This, however, does not preclude the possibility that unionized molecules or intermediate ions may exist, or, indeed, that other complexes may be present in these solutions.

3. *Theories Taking into Account the Interionic Forces.* a. *Theory of Malmström and Kjellin.* A great many investigators have attempted to account for the properties of solutions of electrolytes by taking into account the forces acting between the charges. According to this view, as was pointed out by Thomson [17] and by Nernst,[17a] the ionization of an electrolyte under given conditions should be the greater the greater the dielectric constant of the medium.

Among those who have attempted a solution of the problem by this method are Kjellin [18] and Malmström.[19] These theories, which are practically the same, lead to an equation of the form:

$$A \log C_i = \log K + \log C_u + B C_i^{1/3}$$

[17] Thomson, *Phil. Mag.* [5], *36*, 320 (1893).
[17a] Nernst, *Ztschr. f. phys. Chem. 13*, 531 (1894).
[18] Kjellin, *Ztschr. f. phys. Chem. 77*, 192 (1911).
[19] Malmström, see Kjellin, above.

where A, B and K are constants and C_u and C_i are the concentrations of the ions and the un-ionized molecules, respectively. For binary electrolytes A has a value of approximately 1.5, B of 0.3 and K of 1.0. Applied to aqueous solutions of sodium and potassium chlorides, this equation was found to reproduce the results quite closely up to 0.05 N, the constants of the equation being fitted to the experimental values. Similar results were obtained with a number of ternary salts. The equation is not applicable to solutions in solvents of lower dielectric constant such as ammonia, even at low concentrations. At high concentrations, in solvents of dielectric constant less than 20, it is obviously inapplicable, since, according to this equation, Λ necessarily increases with concentration. It may be noted that the form of this equation resembles somewhat that of Brönsted's for the solubility of a salt in the presence of other salts.

b. *Theory of Ghosh.* The most comprehensive theory which has been proposed to account for the behavior of solutions of electrolytes is that of Ghosh.[20] Ghosh assumes that strong electrolytes are completely ionized, but that only those ions whose energy is sufficiently great to overcome the electrostatic field due to the charges are active in carrying the current. It is difficult to see how Ghosh's activity coefficient differs from the usual ionization coefficient. Apparently, what this author has in mind is that the ionic complexes persist in the neutral molecules. While such an assumption is not fundamental to the older ionic theory, it is nevertheless true that previous investigators[21] in this field have long since recognized that in the neutral molecule the identity of the ionic complexes is not lost. The theory of Ghosh, as well as those of some other writers, would be more readily understandable to most readers if the customary nomenclature had been retained.

Ghosh calculates the potential due to the field on the assumption that the ions are distributed in the medium in a definite manner forming a space lattice. He assumes that the space lattice of a salt in solution corresponds to that of the salt in the crystalline state and therefrom calculates the distance between the positive and negative charges. In calculating the potential, Ghosh assumes that the ions form doublets so that the work involved in separating the ions is due only to the N pairs of positive and negative ions. This theory has been criticized by Partington,[22] Chapman and George,[23] and more recently by Kraus.[24] These

[20] Ghosh, *Trans. Chem. Soc. 113*, 449, 627, 707, 790 (1918).
[21] Noyes, Aqueous Solutions at High Temperatures, Carnegie Publication No. 63, p. 350 (1907).
[22] Partington, *Trans. Faraday Soc. 15*, 111 (1919-20).
[23] Chapman and George, *Phil. Mag. 41*, 799 (1921).
[24] Kraus, *J. Am. Chem. Soc. 43*, Dec., 1921.

criticisms need not be further considered here but it may be of interest to compare the conductance values calculated according to Ghosh's theory with those experimentally determined.

For the conductance of an electrolytic solution Ghosh's theory leads to the following equation:

$$\log \Lambda = \log \Lambda_0 - \frac{\beta C^{1/3}}{DT} \tag{124}$$

where

$$\beta = \frac{NE^2(2N)^{1/3}}{2.3026\, mR}. \tag{125}$$

Here N is Avogadro's number, 6.16×10^{23}, E is the electrostatic unit of charge, 4.7×10^{-10} E.S.U., R is the value of the gas constant in absolute

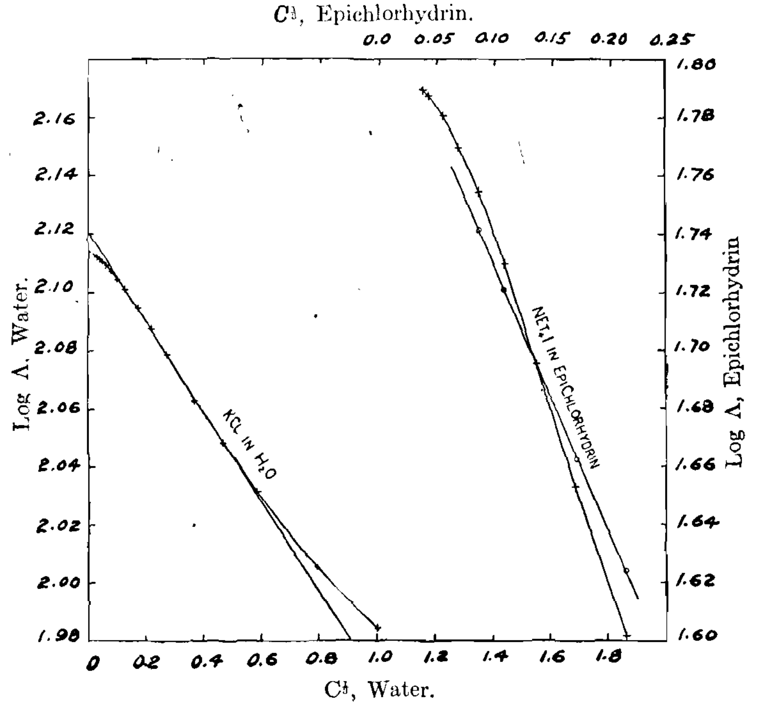

FIG. 61. Plot of Ghosh's Conductance Function for Solutions of Potassium Chloride in Water at 18° and Tetraethylammonium Iodide in Epichlorhydrin at 25°.

units, and m is a factor depending upon the number of ions n resulting from the ionization of the neutral molecules and upon the number of charges associated with a single ion, as well as upon the manner of distribution of these ions in the solvent medium. It is evident that, for a

given solvent at a given temperature, the logarithm of the equivalent conductance is a linear function of the cube root of the concentration and Ghosh's theory may be readily tested by plotting the experimentally determined values of log Λ against those of $C^{1/3}$. If the equation is applicable, the experimental points should lie upon a straight line from which the values of Λ_0 and β may be determined. If the equation is not applicable, the experimental points will evidently show a systematic deviation from a straight line.

In Figure 61 are shown the curves for potassium chloride in water and for tetraethylammonium iodide in *epi*chlorhydrin. It is evident from the figure that the experimental points lie upon a curve concave toward the axis of concentrations at low concentrations and convex toward this axis at higher concentrations, with an inflection point between. The experimental points show a systematic deviation from a linear relation and Ghosh's equation therefore is not applicable. In Table CXXXIII the observed and calculated conductance values are compared.

TABLE CXXXIII.

Comparison of Observed and Calculated Values of Λ for KCl in Water at 18°.

$\Lambda_0 = 132.06 \quad \beta = 3.620 \times 10^3 \quad T = 291 \quad D = 81$

V	5×10^4	2×10^4	10^4	5×10^3	2×10^3	10^3	5×10^2
$\Lambda_{calc.}$	130.80	130.35	129.90	129.35	128.40	127.47	126.30
$\Lambda_{obs.}$	129.51	129.32	129.00	128.70	128.04	127.27	126.24
$\Lambda_{obs.-calc.}$ ...	—1.39	—1.03	—0.90	—0.45	—0.36	—0.20	—0.06

V	2×10^2	10^2	50	20	10	5	2	1
$\Lambda_{calc.}$	124.31	122.37	119.97	116.9	112.1	107.4	99.7	92.7
$\Lambda_{obs.}$	126.24	122.37	119.90	115.6	111.8	107.5	101.3	96.5
$\Lambda_{obs.-calc.}$.	+0.03	±0.00	—0.07	—0.3	—0.3	—0.1	+1.6	+3.8

The experimental values have a relative precision not less than 0.05 per cent. It is evident, from the table, that the theoretical values deviate from the experimental values far in excess of any conceivable experimental error, except at a few points in the immediate neighborhood of the inflection point, which is at about 0.01 normal. As may be seen from the curve for *epi*chlorhydrin, the deviations in this solvent are much greater than in water. It is to be noted, too, that the experimental points again lie upon a curve which is of the same type as that of potassium chloride in water; that is, the curve is concave toward the axis of concentration at low concentrations and convex toward this axis at high con-

centrations. It has been shown that this form of the curve is general and that in solutions of non-aqueous solvents the deviations from Ghosh's equation are much greater than in water, and therefore are far in excess of any possible experimental error.[25]

Ghosh has likewise treated other properties of electrolytic solutions. In view of the fact that his theory fails to account satisfactorily for the relation between the conductance and the concentration of electrolytic solutions, it is unnecessary to consider these properties here.

c. *Milner's Theory.* Of the various theories proposed to account for the properties of electrolytic solutions, that of Milner is perhaps the most noteworthy, since it is comparatively free from arbitrary assumptions. Milner[26] has calculated the virial for a system of positively and negatively charged particles by statistical methods, and therefrom has calculated the influence of the ions on the freezing point of solutions.[26a] He found, in effect, that the virial of a system of charged particles has a finite value, from which the osmotic pressure of the solution may be deduced, and therefrom the freezing point.

In the following table are given values of the van't Hoff factor i for potassium chloride in water calculated by Milner, together with the values of i determined by Adams directly from freezing point measurements.

TABLE CXXXIV.

COMPARISON OF MILNER'S VALUES OF i, WITH THOSE EXPERIMENTALLY DETERMINED.

C	0.005	0.01	0.02	0.05	0.1
i_{Milner}	1.962	1.947	1.926	1.885	1.838
i_{Adams}	1.961	1.943	1.922	1.888	1.861

As may be seen from the table, the calculated values of i are in excellent agreement with those determined by Adams. Milner's values are based on the assumption that the electrolyte is completely ionized, the observed freezing point depression being due entirely to the interaction of the ions. If an ionization value were assumed corresponding to that given by the ratio Λ/Λ_0, the values of i, as calculated by Milner, would be lower than those observed. Milner has accordingly suggested that, within these ranges of concentration, strong electrolytes are completely ionized. If this is so, the change in the conductance of electrolytes must

[25] Kraus, *loc. cit.*
[26] Milner, *Phil. Mag.* 23, 551 (1912) ; *ibid.*, 25, 742 (1913).
[26a] Compare, Cavanagh, *Phil. Mag.* 43, 606 (1922).

be due to a reduction in the mean carrying capacities of the ions at higher concentrations.

Thus far, the conductance of electrolytic solutions as a function of their concentration has not been accounted for with equal success. Milner[27] has considered this problem, but without arriving at an expression for the conductance as a function of concentration. He has concluded, however, that the decrease of conductance at low concentration must be mainly due to a decrease in the ionic mobilities and not to a decrease in their number. The argument here does not appear to be altogether convincing. Milner assumes, for example, that the undissociated molecules are normal in their osmotic behavior. The justification for this assumption is by no means obvious. Moreover, experimental facts weigh heavily against the generality of the conclusion reached. Weak electrolytes in water, and, apparently, all classes of electrolytes in non-aqueous solutions, approach the mass-action law as a limiting form at low concentrations. The difficulty is not alone to account for the failure of the mass-action law in solutions of strong electrolytes in water but, also, to account for the applicability of this law to solutions in other solvents where, judging by the lower value of the dielectric constant, the interionic forces are much greater than in water. Furthermore, according to Milner's theory, different electrolytes in dilute solutions should exhibit practically identical properties both as regards their osmotic and their electrical properties. This condition is approximately fulfilled in water, but not in solutions in non-aqueous solvents. In these latter solvents, the electrolyte appears to retain its individuality even at exceedingly low concentrations. Any theory which cannot give an account of this fundamental property of electrolytic solutions is obviously incomplete.

It is not difficult to see in what manner the conductance would be influenced by interionic action at higher concentrations. According to Milner, the ions are not distributed haphazard throughout the medium, but, on the average, as the result of interaction between the charges, ions having like charges are somewhat farther apart and ions having unlike charges somewhat nearer together than would otherwise be the case. Ordinarily it is assumed that a charged particle moves in a uniform electric field. If, however, the ions are combining and dissociating, or, in any case, if charged particles approach each other sufficiently closely, the surrounding field will be influenced and the speed of the ions will vary for different individuals, depending upon the proximity of other ions. According to this view, the ratio $\gamma = \frac{\Lambda}{\Lambda_0}$ is a measure, not of the number

[27] Milner, *Phil. Mag.* 35, 214 and 352 (1918).

of particles actually engaged in the transport of the current, but of the mean conducting power of the ions. It does not necessarily follow, however, according to this view, that all the ions in solution are at all times acting as carriers of the current.

Lewis and Randall [28] have recently pointed out that the ionization of an electrolyte cannot be defined without some degree of arbitrariness. This difficulty is not one confined to electrolytic solutions. In all systems, in which reaction takes place among a number of constituents throughout the mass of the mixture, the definition of the concentration of the various constituents concerned becomes uncertain. So long as the system is dilute, the concept of concentration is definite; but, when the concentrations reach such values that the forces acting between the constituents become appreciable, the concept embodied in the term molecule becomes indistinct. This difficulty arises of necessity whenever we pass from the purely thermodynamic to the kinetic method of treating systems of real substances. That these various difficulties should arise in solutions of electrolytes is not surprising, since these are the only concentrated systems regarding which we have data sufficiently accurate to enable us to observe the deviations from ideal systems with any considerable degree of certainty. That un-ionized molecules exist in aqueous solutions of ternary salts in water appears to be conclusively demonstrated by the fact that transference measurements have shown that complex cations exist. Thus, the transference number of the cadmium ion, in cadmium iodide, according to Hittorff, is greater than unity at high concentrations, and the manner in which the transference number of cadmium chloride varies with the concentration indicates that its behavior is not essentially different from that of cadmium iodide. It must be assumed, therefore, that, in solutions of cadmium salts, ions of the type CdX^+ exist. If this is true of one electrolyte, the same may well be true of others.

Finally, it is not sufficient that a theory of electrolytic solutions shall account merely for a diminution in the conducting power of electrolytes with increasing concentration, for, in solutions in non-aqueous solvents, the conductance increases with increasing concentration at higher concentrations; and, if the dielectric constant is sufficiently low, the conductance increases with increasing concentration even at relatively low concentrations.

d. *Hertz's Theory of Electrolytic Conduction.* P. Hertz [29] has attempted to solve the problem of electrolytic conduction by taking into account the interionic forces. He has derived the following equation

[28] *Loc. cit.*
[29] Hertz, *Ann. d. Phys.* 37, 1 (1911).

expressing the relation between the equivalent conductance Λ and the *concentration* C of the solution:

$$\psi(u) = u^3\left\{\left[\frac{\pi}{2} - Si(u)\right]^2 + [Ci(u)]^2\right\} \tag{126}$$

where

$$Si(u) = \int_0^u \frac{\sin u}{u}\,du, \tag{127}$$

$$Ci(u) = \int_0^u \frac{\cos u}{u}\,du, \tag{128}$$

$$\psi(u) = B(\Lambda_0 - \Lambda), \tag{129}$$

and

$$u = AC^{1/3} \tag{130}$$

Here Λ_0, A and B are constants. Λ_0 is the limiting value which the equivalent conductance approaches as the concentration decreases indefinitely. This equation is of the form:

$$B(\Lambda_0 - \Lambda) = \psi\,(AC^{1/3}). \tag{131}$$

It is evident that, for a given solvent under given conditions, the conductance function will have the same form for different electrolytes according to this theory. If the values of $\psi\ (u)$ and of u are represented graphically, then it should be possible to transform the curve for one electrolyte into that for another by merely altering the scale of plotting. It is obvious that this condition will be very nearly fulfilled in aqueous solutions of strong binary electrolytes, since the ionization of different electrolytes at lower concentrations is practically identical. If Hertz's theory held strictly, the value of the constant A would be predetermined by the nature and condition of the solvent and would be independent of the nature of the electrolyte. The difference in the values of the conductance of different electrolytes, therefore, would be accounted for by a difference in the values of the constants Λ_0 and B, and the different conductance curves should be transformable one into the other by merely altering the values of these constants; or, if Λ_0 is otherwise determined, by merely altering the value of the constant B.

Lorenz[30] has tested the applicability of Hertz's function to aqueous solutions of binary electrolytes and has concluded that this function is applicable. As has just been pointed out, this was to have been expected. It should be noted, however, that the value of A, according to Lorenz, differs appreciably for different electrolytes. This result may, in part, be due to the fact that the function has been applied at concentrations where the viscosity effects become appreciable.

It is evident that Hertz's function will not be generally applicable to solutions in non-aqueous solvents, certainly not unless the value of A is assumed to differ largely for different electrolytes. Furthermore, it will be entirely inapplicable to solutions in non-aqueous solvents of low dielectric constant at higher concentrations. It is evident from Equation 126 that the factor of u^3 is essentially positive so that $\Lambda_0 - \Lambda$ must necessarily increase with increasing concentration. It is known, however, that, in solvents of low dielectric constant, the value of Λ passes through a minimum, after which the value of $\Lambda_0 - \Lambda$ decreases with increasing concentration. This theory, like others of its kind, is at best restricted in its applicability. As yet it has not been compared with experimental data in a sufficient number of solutions to make it possible to form a clear opinion as to the range of its applicability. In any case, it is inapplicable to solutions in solvents of very low dielectric constant, even though these solutions may be dilute. Here again, as in the case of Milner's theory, the difference in the behavior of strong and weak electrolytes remains to be accounted for.

4. *Miscellaneous Theories.* A great many other theories have been suggested to account for the behavior of electrolytic solutions. In general, these theories have not been worked out sufficiently to comprehend within their scope more than a limited number of properties of a limited number of systems. Many of them, indeed, are purely qualitative in character.

To account for the increase in the conductance of solutions of electrolytes in solvents of very low dielectric constant, Steele, MacIntosh and Archibald[31] have suggested that at higher concentrations the electrolyte polymerizes, and that only these polymerized molecules are capable of ionization. They show that, if a sufficient degree of polymerization is assumed, an ionization curve is obtained somewhat similar in form to that of ordinary electrolytes in aqueous solution. Thus far, this theory is purely qualitative in character and an exact test of its applicability is therefore not possible. We should expect, however, that if only

[30] Lorenz and Michael, *Ztschr. f. anorg. Chem.* *116*, 161 (1921); Lorenz and Neu, *ibid.*, *116*, 45 (1921); Lorenz and Osswald, *ibid.*, *114*, 209 (1920).
[31] Steele, MacIntosh and Archibald, *Phil. Trans.* [A] *205*, 99 (1905).

polymerized molecules were capable of ionization, intermediate ions would be present in solution and transference measurements with such solutions, therefore, should yield very abnormal values for the transference numbers. While certain transference numbers are unquestionably abnormal and while it is indeed very probable that polymerization often occurs in solutions of electrolytes in solvents of both high and low dielectric constant, it remains to be shown that the phenomenon is a general one and that it is capable of accounting for the observed properties of electrolytic solutions. Nevertheless, it is highly probable that the effect of polymerization will have to be taken into account in many cases at higher concentrations. It appears, however, that polymerization should lead to a lower rather than to a higher value of the conductance. Transference measurements with the alkali metal halides in acetone yield abnormally high values for the cations, indicating the formation of a complex cation. It is to be noted, however, that the conductance of the halide is the lower the greater its tendency to form complexes. Thus, the conductance of lithium chloride in acetone at higher concentrations is much lower than that of potassium iodide or sodium iodide. That complex ions are formed in solutions of cadmium iodide in water was shown by Hittorf, as has already been pointed out. The assumed ionization process in solutions of electrolytes is in a large measure hypothetical. This may account for numerous discrepancies at higher concentrations.

Other writers consider solutions of strong electrolytes to be similar to solutions of colloids. Among these are Reychler,[32] Georgievics [33] and Wo. Ostwald.[34] These theories, however, appear to be little more than analogous, based chiefly upon the similarity between the Storch equation and the adsorption equation. The Storch equation is only an approximation in aqueous solutions which, in other solvents, fails entirely. The osmotic effects in solutions of electrolytes, also, are not in harmony with the view that solutions of strong electrolytes are colloidal in character.

Some writers attempt to account for the properties of aqueous solutions by taking into account reactions between the solvent and the electrolyte. In this connection, it is to be noted that electrolytic solutions are not confined to solvents of the water type. Indeed, such solvents need not necessarily contain hydrogen and, in fact, may be elementary substances, or neutral carbon compounds such as chloroform. In view of this fact, it is highly improbable that the properties of electrolytic solutions may be generally accounted for on the basis of chemical processes

[32] Reychler, "Etude sur l'Equilibre de Dissociation," Brochure No. 3, Bruxelles (1917), H. Lamertin.
[33] Georgievics, *Ztschr. f. phys. Chem.* *90*, 356 (1915).
[34] Ostwald, *Ztschr. Chem. Ind. Koll.* *9*, 189 (1911).

taking place between the solvent and the dissolved electrolyte. But here, again, there are doubtless many instances where interaction between the electrolyte and the solvent or an added non-electrolyte is a primary factor in the ionization process, particularly at higher concentrations.

5. *Recapitulation.* In recapitulation, solutions of strong electrolytes, even at low concentrations, do not conform to the laws of dilute systems. The thermodynamic properties of these solutions can not, therefore, be employed for the purpose of determining the state of the electrolyte in these solutions. The conductance method might be expected to give a measure of the fraction of the ionized and un-ionized molecules present. However, the fact that the relative conductance of the ions of strong acids varies at low concentrations renders the results of the conductance method doubtful.

The hypothesis that electrolytes are completely ionized up to fairly high concentrations lacks experimental support. The agreement of the hypothesis with the consequences of thermodynamic principles can not be looked upon as lending material support, since thermodynamics can teach us nothing with regard to the molecular state of a system without a supplementary hypothesis which directly or indirectly involves the equation of state. The fact that the law of mass-action is approached as a limiting form in aqueous solutions of weak electrolytes and in non-aqueous solutions of all electrolytes for which reliable data are available indicates that, if strong electrolytes in aqueous solution are completely ionized, this constitutes only a particular case and the general problem still remains to be solved.

Any theory which undertakes to account for the decreased conductance of electrolytes at higher concentrations, on the assumption that the conductance change is due to a change in the speed of the ions, must likewise account for the fact that, in solvents of low dielectric constant, the conductance passes through a minimum value after which it increases. This point may lie at relatively low concentrations.

The theories of electrolytic solutions thus far advanced are founded chiefly on observations relating to aqueous solutions. There is great danger, here, that phenomena may be assumed as general which, in fact, are only particular. It is of the greatest importance to analyze the results obtained from a study of the properties of solutions in various solvents in order to determine which of these are general, applying to all electrolytic solutions, and which are particular, applying only to solutions in certain solvents or under certain conditions. Aqueous solutions are characterized by the uniformity of the phenomena presented by different electrolytes. In other words, the electrolyte, in aqueous solution, has,

in a large measure, lost its individuality. This is not true of solutions in other solvents. Here the electrolyte retains its individual characteristics even at very low concentrations. It is interesting to note that, at higher temperatures, certain of the individual properties of electrolytes in aqueous solution disappear while others make their appearance. Thus, the ionic conductances approach one another at higher temperatures, while the ionization values diverge the more the higher the temperature. It is not to be doubted that the properties of aqueous solutions at higher temperatures closely resemble those of non-aqueous solutions under ordinary conditions.

It is not unlikely that, in the end, many of the theories, which have been suggested from time to time and found inapplicable, contain certain elements of truth. The error has been introduced in attempting to apply, generally, theories which are applicable only to special cases. It appears probable that, ultimately, it will be necessary to take into account, under various conditions, a change in the speed of the ions with concentration as well as a change in the degree of ionization. At the same time there will doubtless be found many cases in which intermediate ions are formed and in which the electrolyte polymerizes. Yet there is found, in all electrolytic solutions, a certain unity among the phenomena, which indicates the existence of a comparatively small number of chief governing factors.

Chapter XIII.

Pure Substances, Fused Salts, and Solid Electrolytes

1. *Substances Having a Low Conducting Power.* In the preceding chapters, the properties of solutions of electrolytes have been discussed. We shall now consider, briefly, the properties of pure substances in the liquid state. Nearly all substances in the fused condition exhibit a measurable, though often small, conducting power for the electric current. Even such substances which we ordinarily class as insulators conduct the current in some degree. What the nature of the conduction process is in these substances has not been shown, but in all likelihood the process is an ionic one; that is, the current is carried by particles of atomic or molecular dimensions. A typical example of this class of conductors, or perhaps more properly insulators, is found in the hydrocarbons. It has been shown that the conductance of substances of this type is materially affected by the presence of small amounts of impurities. The specific conductance of nearly all poorly conducting substances is materially decreased by careful drying and fractionation. Evidently, therefore, in part at least, the conductance of this class of substances is due to the presence of other substances, as a result of which their conductance is materially increased. We have, however, no knowledge of the nature of the charged particles by means of which conduction is effected.

In the case of petroleum ether and hexane, it has been found possible to carry the process of purification so far that the effect of impurities is almost entirely eliminated. It has been found that the residual conductance in these solvents is chiefly due to the action of radiations from surrounding bodies, as a result of which the solvent itself is ionized.[1] The conductance under these conditions was found to be altered by surrounding the conductance vessel with screens which absorb the external radiation. The conductance of pure hexane, therefore, is lower than that due to the ions produced by the radiation from surrounding bodies and it is possible that the conductance of this substance is in effect zero. Under ordinary conditions, the conductance of the hydrocarbons is due primarily to impurities.

[1] Jaffé, *Ann. d. Phys.* 32, 148 (1910).

Recent investigations on the conduction process in solid dielectrics have disclosed the fact that in these media Ohm's law is not obeyed.[2] The substances investigated were mica, glass, paraffin, shellac and celluloid. Excepting paraffin, for which the conductance was so low that the results were uncertain, the conductance was found to increase with the applied potential. The logarithm of the specific conductance increases approximately as a linear function of the potential gradient. In the case of mica, with which substance measurements were made over a large range of potential, the conductance curves are slightly concave toward the axis of potentials. In the case of glass the conductance increase at higher temperatures was found to be noticeably smaller than at lower temperatures.

Since Ohm's law does not hold, it must be assumed either that the number of carriers increases with the applied potential or that the mean speed of the carriers increases. It is not improbable that, under the action of the applied potential, carriers of a type differing from those normally present in the dielectric medium may be formed. It is of particular interest to note that in glass, which is an electrolyte at higher temperatures, the above mentioned results indicate a conduction process differing from that at higher temperatures.

Compounds of hydrogen with elements which are strongly electronegative are in general ionized to a slight degree. The most familiar example of this type is water itself, which in the pure state has a specific conductance in the neighborhood of 0.042×10^{-7}.[2a] Other hydrogen derivatives of strongly electronegative groups likewise appear to conduct the current in the pure state, some of them much more readily than water. The specific conductance of formic acid appears to lie in the neighborhood of 10^{-5}. In these cases, however, the process of purification has not been carried to such a point that it can with certainty be stated that the residual conductance is entirely or chiefly due to the ionization of the solvent alone. In the case of hydrogen derivatives, in which the hydrogen is not joined to a strongly electronegative group, the residual specific conductance is as a rule relatively low and it is as yet uncertain to what the residual conductance is due. Acetone, for example, may be purified to a point where its specific conductance is of the order of 10^{-8}, but whether this residual conductance is due to acetone itself or to some impurity is unknown. The same obviously holds true of solvents which contain no hydrogen, such as sulphur dioxide, bromine, etc.

The hydrogen derivatives of the strongly electronegative groups are

[2] Poole, *Phil. Mag.* 42, 488 (1921).
[2a] Kohlrausch and Heydweiller, *Ann. d. Phys.* 83, 209 (1894).

perhaps to be classed as salts. In other words, these compounds should be classed, not with the ordinary hydrocarbons, but rather with the distinctly salt-like substances. These derivatives, when dissolved in water, or other suitable solvents, yield solutions which conduct the current with great facility and which often form compounds with the solvent. Hydrochloric acid forms a stable complex, ammonium chloride, with ammonia; and with water at low temperature it has been shown to form a complex $HCl.H_2O$.[3] In water itself, therefore, hydrogen and hydroxyl ions do not consist merely of a hydrogen atom and an OH group associated with the positive and negative charge respectively, but rather of complexes in which the solvent itself is involved. In a sense, therefore, water and ammonia and hydrogen chloride may be considered to be related to salts. However, the typical salts in a fused state exhibit in most instances a conductance much greater than that of the substances which we have just been discussing.

With a few exceptions, fused salts conduct the current with extreme facility. Among these exceptions mercuric chloride is one of the most common and striking examples. This salt is itself an electrolytic solvent for other salts, while its specific conductance in the pure state is very low.[4] Correspondingly, solutions of mercuric chloride in other solvents, as for example water, appear to be only slightly ionized. This class includes the organic tin salts of the type R_3SnX. Trimethyltin iodide, for example, is a liquid at ordinary temperatures whose conductance is less than 4×10^{-5}. This salt when dissolved in water is ionized normally.[5]

2. *Fused Salts.* Inorganic substances which are non-electrolytes in solution, in general, possess only a very low conducting power in the pure state. This, for example, is the case with boric oxide. On the other hand, oxides of the strongly electropositive elements appear to be conductors in the fused or even in the solid state. It is, however, the typical salts in their fused state which are of greatest interest. These substances, in general, conduct the current with extreme facility, by means of a purely ionic process, since, as has been shown, Faraday's law applies.

In Table CXXXV are given values of the specific conductance μ of sodium nitrate at different temperatures, together with the equivalent conductance Λ as calculated from the known specific volume, the fluidity of the fused salt F, and the ratio of the conductance to the fluidity $\frac{\Lambda}{F}$.[6]

[3] Rupert, *J. Am. Chem. Soc. 31*, 851 (1909).
[4] Foote and Martin, *Am. Chem. J. 41*, 45 (1909).
[5] Unpublished observations by Mr. C. C. Callis in the Author's Laboratory.
[6] Goodwin and Mailey, *Phys. Rev. 25*, 469 (1907); *ibid., 26*, 28 (1908).

TABLE CXXXV.

Conductance and Fluidity of Sodium Nitrate at Different Temperatures.

t	μ	Λ	F	Λ/F
350°	1.173	52.87	42.6	1.24
400	1.384	63.59	54.0	1.18
450	1.562	73.15	65.0	1.12
500	1.716	81.94	77.2	1.06

It will be observed that the specific conductance μ, as well as the equivalent conductance Λ, increases very nearly as a linear function of the temperature. Obviously, the equivalent conductance will vary nearly in proportion to the specific conductance, since the density of the fused salt varies only comparatively little with temperature. Between 350° and 500°, the specific conductance increases approximately 60 per cent, which corresponds roughly to an increase of ½ per cent per degree. The fluidity varies somewhat more than the conductance over the same temperature interval, so that, as the temperature rises, the value of the ratio $\frac{\Lambda}{F}$ decreases. It is interesting to note that the value of $\frac{\Lambda}{F}$ is near unity, which differs not greatly from the value of $\frac{\Lambda}{F}$ for electrolytic solutions, particularly in the case of water. This may be taken to indicate that the fused salts are highly ionized.

For different fused salts, the conductance is of the same order of magnitude, corresponding to the fact that they have approximately the same fluidity. In Table CXXXVI are given values of the specific conductance μ, the equivalent conductance Λ, and the fluidity F, together with the ratio $\frac{\Lambda}{F}$ for different salts. It will be observed that the ratio

TABLE CXXXVI.

Values of Λ and F for Different Fused Salts.

		μ	Λ	F	Λ/F
350°C.	$NaNO_3$	1.173	52.88	42.6	1.24
"	KNO_3	0.6728	36.54	38.0	0.96
"	$AgNO_3$	1.245	55.43	45.5	1.22
310°C.	$LiNO_3$	1.126	44.21	27.2	1.62
250°C.	$AgClO_3$	1.4743	27.72	..	..

$\frac{\Lambda}{F}$ is of the same order for the different salts. In the case of the nitrates the ratio is smallest for potassium nitrate and greatest for lithium nitrate. The order of the ratio $\frac{\Lambda}{F}$ corresponds to the order of the atomic volumes,

Jaeger and Kapma[6a] have measured the specific conductance and the densities of potassium nitrate, sodium nitrate, lithium nitrate, rubidium nitrate, caesium nitrate, potassium fluoride, potassium chloride, potassium bromide, potassium iodide, sodium molybdate, and sodium tungstate over considerable temperature ranges. At a given temperature, the equivalent conductance of the different salts is of the same order of magnitude. For the nitrates the conductance increases in order from caesium to lithium. For the potassium halide salts, the conductance is smallest for the fluoride and greatest for the chloride, while that of the iodide and bromide is intermediate between them.

The conductance increases very nearly, although not quite, as a linear function of the temperature. The temperature coefficients vary appreciably, being greatest for potassium fluoride and smallest for caesium nitrate.

The conductance of mixtures of fused salts is very nearly a linear function of the composition. In the following table are given values of the conductance of mixtures of sodium and potassium nitrates at 450°, together with the values of F and of $\frac{\Lambda}{F}$.[7a] It will be observed that as the concentration changes the conductance varies continuously between that of the two components.

TABLE CXXXVII.

CONDUCTANCE OF MIXTURES OF SODIUM AND POTASSIUM NITRATES AT 450°.

	0	20	50	80	100 molar % KNO_3
μ ..	1.562	1.389	1.205	1.059	0.973
Λ ..	73.15	67.84	62.56	57.96	55.03
F ..	65.7	..	66.3	63.3	60.2
Λ/F ..	1.12	..	0.945	0.915	0.915

The fact that in the mixtures of fused salts the conductance is approximately a linear function of the composition shows that no considerable reaction takes place on mixing. This indicates a high degree of ionization of the fused electrolyte.

In Table CXXXVIII are given values of the conductance of mixtures of silver iodide and silver bromide at 550°.[7] Here, again, the conduc-

TABLE CXXXVIII.

CONDUCTANCES OF MIXTURES OF SILVER IODIDE AND SILVER BROMIDE.

%AgBr	0	5	10	20	30	40	60	70	80	90	100
μ	2.36	2.40	2.39	2.41	2.43	2.50	2.64	2.67	2.68	2.84	3.00

[6a] Jaeger and Kapma, *Ztschr. f. Anorg. Chem.* *113*, 27 (1920).
[7a] Goodwin and Mailey, *loc. cit.*
[7] Tubandt and Lorenz, *Ztschr. f. phys. Chem.* *87*, 543 (1914).

tance varies continuously between that of the two components. It is true that a few irregularities occur, but these are small and probably lie within the limits of experimental error. The fused salts are characterized by the great similarity in their behavior. As has already been pointed out, the order of magnitude of the conductance is the same for all typical fused salts.

In the following table are given values of the conductance of thallium and silver salts at 600°.[8]

TABLE CXXXIX.

CONDUCTANCE OF THALLOUS AND SILVER SALTS AT 600°.

TlI	0.840	AgI	2.43
TlBr	1.127	AgBr	3.08
TlCl	1.700	AgCl	4.16

In both cases, the conductance of the salt increases in the order: iodide, bromide, chloride. The conductance of the silver salts is markedly greater than that of the thallium salts.

A great many data are available relating to the conductance of fused salts,[9] but, in view of the similarity in the behavior of the different fused salts, it is unnecessary to give here in detail the various observations which have been recorded. Thus far, the subject has been studied chiefly from an empirical point of view and we possess but little knowledge of the molecular condition of these substances.

The form of the conductance curve of mixtures of sodium and potassium nitrate and of silver chloride, iodide and bromide indicates that in these mixtures complex ions are not formed. In some other instances, however, there is a probability that complex ions may exist.[10] This is the case, for example, with mixtures of potassium chloride and lead chloride. Lorenz has carried out transference measurements which indicate that a complex of the type K_2PbCl_4 is probably formed in the mixture.

3. *Conductance of Glasses.* For want of a suitable reference substance, transference measurements with the fused salts have not been carried out, and as a consequence we lack any knowledge as to the proportion of the current carried by the two ions in these electrolytes. In a few instances, however, particular systems have been investigated in which the current is carried entirely by either the positive or the nega-

[8] Tubandt and Lorenz, *loc. cit.*
[9] Lorenz, "Electrolyse geschmolzener Salze, Monographien u. Angew. Electroch," 20 (1905).
[10] Lorenz, *Ztschr. f. phys. Chem.* 70, 230 (1910).

tive ion. Among those substances which may be classed strictly as fused salts are the glasses. A glass is to be considered as a supercooled liquid which is mechanically rigid. Usually, glasses consist of mixtures of silicates of the alkali metals and the metals of the alkaline earths. What the nature of the compounds is in these systems is not known. Doubtless, the silica is present in the electronegative constituent. It is well known that ordinary glasses are excellent conductors of the current at high temperatures, the conductance increasing with the temperature. In general, the conductance-temperature curve is exponential in form.

In the following table are given values of the resistance of ordinary soda-lime glass at different temperatures.[11]

TABLE CXL.

RESISTANCE OF ORDINARY SODA GLASS AT DIFFERENT TEMPERATURES.

Temperature C....	325	355	404	469	484	500	540
Resistance	9200	1900	687	172	133	89	2.4

It will be observed that, even at temperatures as low as 325°, glass conducts the current with measurable facility, while in the neighborhood of its softening point, 540°, it conducts extremely well. To what the great increase in the conductance of glass is due is uncertain. We shall see below that the ionization of a glass varies only little as a function of the temperature and consequently the increased conductance must be due to the increased speed of the ions. The nature of the frictional resistance which the ions meet in their motion through a glass is, however, uncertain. At temperatures below 400°, glasses of this type appear to be entirely rigid and consequently the increased conductance is not simply related to the mechanical rigidity of the glass.

The conduction process in the case of the glasses is electrolytic in character.[11a] If a current is passed through a glass tube from a sodium nitrate anode to a mercury cathode, metal is transferred from the sodium nitrate to the mercury through the glass in accordance with Faraday's law and no change whatever takes place in the glass itself. This indicates that the conduction process in such glasses is due to the motion of the sodium ion and is not due to the motion of an electronegative ion. This type of conduction is characteristic of many rigid electrolytic conductors. Since positively charged carriers are present within the glass, it is obvious that negative carriers must likewise be present. The negative carriers, however, must form a substantially rigid system, since they take no part in the conduction process. It is also evident that, in the

[11] Darby, Thesis, Clark University (1917).
[11a] LeBlanc and Kerschbaum, *Ztschr. f. phys. Chem.* 72, 468 (1910).

case of the glasses, the ions consist of the atoms themselves, since, on passing a current through soda-lime glass, the only material transferred is sodium. This and similar cases are the only ones in which it has been definitely demonstrated that an electrolytic ion consists of a charged atom alone.

In the case of glasses, it is possible to substitute the sodium ion by another positive ion.[11b] Such a substitution is, in effect, a determination of the speed of the ions by the moving boundary method. Substitution may be quite generally effected but, in the case of most positive ions, the glass disintegrates as the process proceeds. In the case of silver, however, a substitution may be carried out to a considerable depth. If sodium is substituted by silver, the weight of the glass is increased in proportion to the difference in the atomic weight of silver over that of sodium. In the following table are given values of the gain in weight of a sample of soda glass, together with the values calculated from the amount of electricity passed as determined in a coulometer.[11c] The temperature is given in the first column.

TABLE CXLI.

OBSERVED AND CALCULATED GAIN IN WEIGHT OF SODA GLASS ON SUBSTITUTION BY SILVER.

Temperature	Gain in Weight Calculated	Gain in Weight Observed
350°	0.0339 g.	0.0347 g.
350°	0.0396	0.0416
343°	0.0732	0.0762
343°	0.0209	0.0209

By measuring the penetration of the silver boundary into the glass under a given potential gradient, it is possible to determine the volume of the glass which has been affected, and, knowing the composition of the glass, it is possible to determine the fraction of sodium in the glass replaced by silver. This has been done in the case of soda glass with the following results.[11c]

TABLE CXLII.

RELATIVE AMOUNTS OF SODIUM REPLACED BY SILVER IN SODA GLASS.

t	$\gamma\%$
278°	76.5
295°	76.8
323°	77.05
343°	82.3

[11b] Heydweiller and Kopfermann, *Ann. d. Phys.* **32**, 729 (1910).
[11c] Darby, *loc. cit.*

While these values are not very precise, nevertheless, they clearly indicate that about three-fourths of the sodium present in these glasses may be electrolyzed out and replaced by another metal. The effective ionization of the sodium in soda glass, therefore, is of the order of magnitude of 75 per cent. This is apparently the only direct determination which has thus far been made of the relative amount of a substance actually concerned in the conduction process in an electrolyte. If so large a proportion of the sodium in soda glass is actually concerned in the conduction process, it is reasonable to assume that the fused salts are very nearly completely ionized. It is interesting to note that, as the temperature rises, the ionization of sodium in glass increases slightly.

Since the penetration of the silver is determined solely by the rate of motion of the ions and since the conduction is due entirely to the positive ion, it follows that the depth of penetration should be proportional to the specific conductance or inversely proportional to the specific resistance of the glass. This condition is in general fulfilled.

From the preceding data it is possible to calculate the speed of the sodium ion in glasses; that is, the speed with which this ion moves under a potential gradient of one volt per centimeter. In the following table are given values of the absolute speed of the sodium ion at different temperatures.

TABLE CXLIII.

Absolute Speed of the Sodium Ion in Soda Glass at Different Temperatures.

278°	4.52×10^{-8}
295°	1.46×10^{-7}
323°	3.26×10^{-7}
343°	5.9×10^{-6}

It will be observed that, as might be expected, the absolute speed of the sodium ion is relatively very low. On the other hand, corresponding to the greatly increased conductance of glass with increasing temperature, the speed of the sodium ion increases largely with temperature.

4. *Solid Electrolytes.* Solid substances, both crystalline and amorphous, conduct the electric current with more or less facility. In the case of the insulators, where the conductance is of an extremely low order, it is not unlikely that conductance is due to the presence of traces of impurities. The only substance for which this has actually been shown is crystalline quartz, in which the conductance is due to the presence of traces of sodium as impurity.[12] Here the current is carried by

[12] Warburg and Tegetmeier, *Ann. d. Phys.* 35, 455 (1888).

the sodium ion which alone is capable of motion in these crystals. The process of conduction appears to be entirely similar to that in glasses.

The typical salts, below their melting point, conduct the current, in some cases, with extreme facility. As a rule, the conductance increases with increasing temperature according to an exponential curve. The specific conductance may be expressed fairly well as a function of temperature by means of the equation:

$$\log \mu = a + bt, \tag{132}$$

where a and b are constants. In the following table are given values of the specific conductance of a few salts at temperatures through their melting points.[13]

TABLE CXLIV.

CONDUCTANCE OF SALTS THROUGH THE MELTING POINT.

TlCl t	TlCl μ	AgCl t	AgCl μ
250°	0.00005	250°	0.00030
300	0.00024	300	0.0015
350	0.0009	350	0.0065
400	0.0037	400	0.026
427 (M.P.)	{0.0067 {1.082	450	0.11
		455	M.P.
450	1.17	456	3.76
500	1.332	500	3.91
600	1.700	600	4.16

AgBr t	AgBr μ	AgI t	AgI μ
200°	0.00052	125°	0.00011
240	0.0023	140	0.00026
280	0.0091	144.6	{0.00034 {1.31
350	0.08		
400	0.38	150	1.33
419	0.51	250	1.78
422	M.P.	350	2.14
425	2.76	450	2.41
500	2.92	550	2.64
600	3.08	552	M.P.
		554	2.36
		600	2.43
		650	2.47

[13] Tubandt and Lorenz, *Ztschr. f. phys. Chem.* 87, 513 (1914).

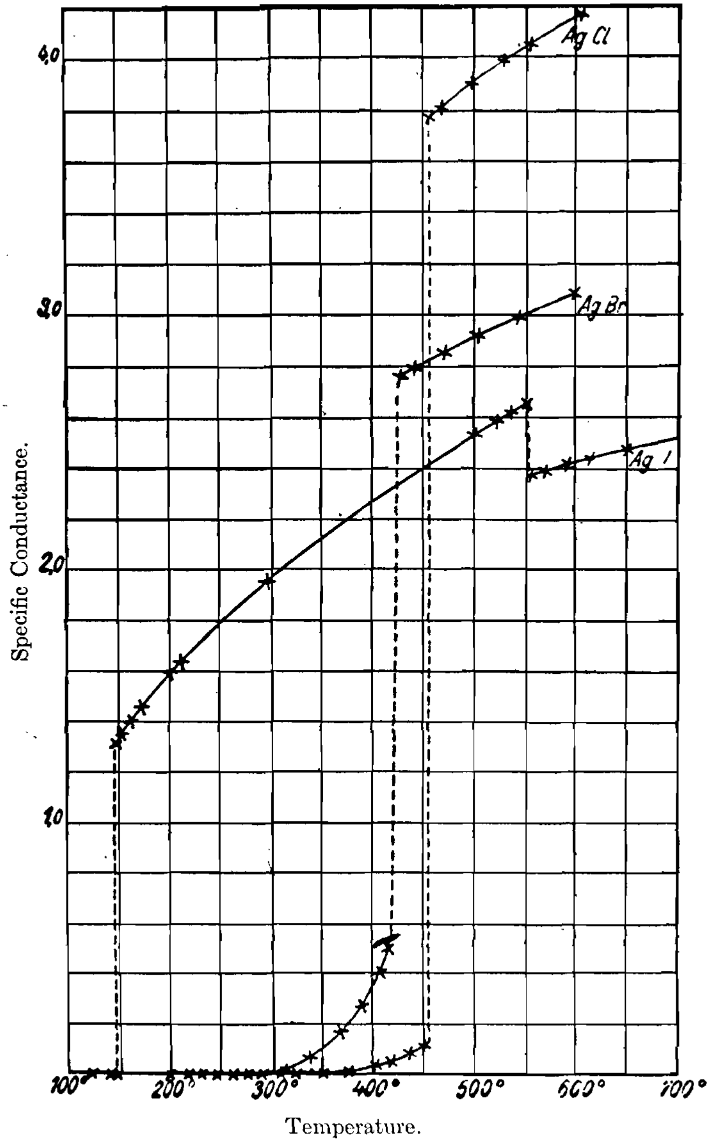

FIG. 62. Specific Conductance of Silver Halides at Various Temperatures Through Their Melting Points.

The relation between the conductance and the temperature is shown graphically in Figure 62. In general, the conductance of the solid salt increases with temperature according to Equation 132 up to the melting

point, where a discontinuity occurs, a large increase taking place on fusion. Silver iodide, however, forms an exception to this rule. This substance exhibits a transition point at 144.6°. Below this temperature the conductance of silver iodide increases with temperature in a manner similar to that of silver chloride and bromide. At the transition point, the specific conductance increases from a value of 3.4×10^{-4} to 1.31. Beyond the transition point, the conductance of silver iodide increases slowly with the temperature, the temperature coefficient being not greatly different from that of fused salts, as may be seen from the figure. It will be observed, furthermore, that at the melting point the conductance of solid silver iodide is markedly higher than that of the fused salt, the conductance on melting decreasing from 2.64 to 2.36. Even at the transition point, at a temperature as low as 144.6, the specific conductance of solid silver iodide is of the order of magnitude of that of fused salts. This is a remarkable phenomenon and shows that the power of conducting the current with facility is by no means restricted to the liquid state. Thus far, however, silver iodide is the only solid salt whose conductance in the solid state has been found to be comparable with that in the liquid state far below its melting point.

The conduction process in solid salts of this type is purely electrolytic, as follows from the fact that Faraday's Law holds true within the limits of experimental error. In the following table are given the observed amounts of silver precipitated on electrolysis, together with the amounts of silver precipitated in a silver coulometer carrying the same current.[14]

TABLE CXLV.

TEST OF FARADAY'S LAW IN SOLID ELECTROLYTES.

Electrolyte	Temperature	Ag Dissolved at Anode	Ag Precipitated in Coulometer	% Dif.
Silver Iodide	540°	0.7212	0.7139	+ 1.20
" "	540	0.5642	0.5623	+ 0.34
" "	150	0.7841	0.7804	+ 0.48
" "	150	0.7767	0.7706	+ 0.80
Silver Bromide	400	0.5883	0.5842	+ 0.70
Silver Chloride	430	0.3779	0.3751	+ 0.75

Considering the small amount of silver precipitated or dissolved and the difficulty of carrying out the experiments, the agreement between the observed and the calculated values of the amount of silver dissolved

[14] Tubandt and Lorenz, *loc. cit.*

at the anode is remarkably good. The applicability of Faraday's Law has been further verified by Tubandt and Eggert.[15] There can be little question but that, in the case of these salts, Faraday's Law holds true.

By employing solid silver iodide above its transition point in contact with a silver cathode, Tubandt[16] has found it possible to test Faraday's law in the case of other electrolytes than the silver salts and, furthermore, has been able to carry out transference measurements in order to determine to what extent the conductance in solid electrolytes is due to the positive and to what extent it is due to the negative carrier. It has been shown that for silver iodide, silver bromide, silver chloride, silver sulphide, above its transition point, and copper sulphide (Cu_2S), Faraday's Law holds and that in these salts the current is carried entirely by the positive ion. These results are very significant in that they show that one set of ions in these solids forms a fixed framework through which the other ions move with considerable facility. In the above salts, the negative ions form the framework through which the positive ions move. In lead chloride, however, the current is carried by the negative ion; the positive ions form the framework through which the negative ions move. These facts have an important bearing on the theory of the structure of solid salts.

Silver sulphide has a transition point at 179°. Above the transition temperature, as was shown by actual electrolysis of the salt, Faraday's Law holds and the current is carried entirely by the positive ions. Below the transition temperature, the β form of silver sulphide appears to conduct in part metallically. In the β form of silver sulphide, Faraday's Law does not hold, only about 80 per cent of the current being carried by the silver ion. The negative ion in this case is apparently not involved in the conduction process, the remainder of the current being carried by a metallic process of conduction. Apparently, therefore, solid electrolytes exist in which the current is carried partly metallically and partly electrolytically. As we shall see in a subsequent chapter, solutions of the alkali metals in liquid ammonia likewise conduct the current by a mixed process.

The conductance of a heterogeneous mixture of two solid electrolytes is approximately a linear function of the composition of the mixture. When two solid electrolytes form mixed crystals, however, the conductance of the homogeneous mixture is often much greater than that of the pure constituents. In the following table are given values of the

[15] Tubandt and Eggert, *Ztschr. f. anorg. Chem.* *110*, 196 (1920).
[16] Tubandt, *Ztschr. f. Electroch.* *26*, 358 (1920).

specific conductance $\mu \times 10^6$ of mixtures of sodium chloride and potassium chloride at 570°.[17]

TABLE CXLVI.

CONDUCTANCE OF MIXTURES OF SODIUM AND POTASSIUM CHLORIDE AT 570°.

% NaCl	0	10	20	30	40	50	60	70	80	90	100
$\mu \times 10^6$	0.87	8.0	16.5	22.0	24.0	24.0	30.0	34.5	40.0	28.0	4.5

The conductance value of 0.87 for pure potassium chloride at 570° has been calculated from the conductance values at somewhat higher temperatures by means of Equation 132. It will be observed that the conductance curve exhibits a maximum in the neighborhood of 80 per cent of sodium chloride, at which point the conductance of the mixture is nearly ten times that of pure sodium chloride and forty times that of pure potassium chloride. Apparently, the maximum lies toward the side of that component which possesses the higher conductance. Other systems of mixed crystals have yielded similar results. Apparently, therefore, it is a general rule that the conductance of mixed crystals is much greater than that of the pure components.

In the case of mixtures of silver iodide with silver bromide and with silver chloride, the conductance-temperature curve of the resulting mixture exhibits discontinuities as a result of the peculiar nature of silver iodide.[18] Up to 80 per cent of silver bromide, a homogeneous phase results initially, whose conductance curve corresponds with that of silver iodide above the transition temperature of 146.5°. Apparently, then, in these mixed crystals, the silver bromide is present in a condition similar to that of silver iodide above its transition point. The details of the conductance curves of these mixtures need not be discussed further here. It may be noted, however, that a study of the conductance of various solid systems is capable of throwing light on the phase relations in these systems.

It will be evident from the foregoing discussion that solid electrolytes exhibit a marked variety of phenomena which have an important bearing on our conceptions of the nature of the conduction process, as well as upon that of the structure of solid salts. The available data are as yet extremely meager, but it may be expected that, as this field is further developed, results of great value will be obtained.

5. *Lithium Hydride.* The conductance of lithium hydride, both in the solid and in the liquid condition, has been investigated by Moers.[19]

[17] Benrath and Wainoff, *Ztschr. f. phys. Chem.* 77, 257 (1911).
[18] Tubandt and Lorenz, *loc. cit.*
[19] Moers, *Ztschr. f. anorg. Chem.* *113*, 179 (1920).

In the following table are given values of the specific conductance of lithium hydride at different temperatures.

TABLE CXLVII.

SPECIFIC CONDUCTANCE OF LITHIUM HYDRIDE AT DIFFERENT TEMPERATURES.

t	μ	t	μ
443°	2.124×10^{-5}	661.5°	2.018×10^{-2}
507	2.113×10^{-4}	685	3.206×10^{-2}
556	8.447×10^{-4}	725	7.596×10^{-2}
570	1.491×10^{-3}	734	1.125×10^{-1}
597	3.225×10^{-3}	754	1.01
638	1.139×10^{-2}		

The values of the specific conductance may be represented by means of a sum of terms in ascending powers of the temperature. It is interesting to note that the same equation applies both above and below the melting point of lithium hydride, which is 680°. Apparently, therefore, there is no discontinuity in the conductance of this hydride at its melting point. This behavior is exceptional.

This salt exhibits polarization when a direct current is passed through it, and it has been shown that, on the passage of the current, lithium is deposited at the cathode and hydrogen evolved at the anode. The current is therefore conducted by either one or both of the ions Li^+ and H^-. This salt, therefore, presents a very interesting case, not only in that the conductance of the solid is the same as that of the liquid at its melting point, but, also, in that hydrogen appears here as a negative ion. This is the only case so far observed in which hydrogen has been shown to function in this manner.

The behavior of hydrogen in lithium hydride is thus very similar to that of certain metallic elements in their compounds with the alkali metals in liquid ammonia, referred to in a preceding chapter. We saw there that, for example, in a solution containing lead and sodium, lead is dissolved at the cathode and precipitated at the anode. In the presence of very electropositive elements, less electropositive elements tend to take up negative electrons and function as anions. This dual function of many elements, which ordinarily act as cations, is very significant from the standpoint of the constitution of many compounds in which these elements are involved.

Chapter XIV.

Systems Intermediate Between Metallic and Electrolytic Conductors.

1. *Distinctive Properties of Metallic and Electrolytic Conductors.* Substances which possess the power of conducting the electric current are, in the main, sharply divided into two classes; namely, metallic and electrolytic conductors. The members of each of these two classes of conducting substances have many properties in common with one another, which properties serve to distinguish the members of one class from those of the other. It is in their optical and electrical properties that the members of the two classes exhibit the greatest contrast. While electrolytic systems, in general, are transparent, metallic systems are non-transparent and exhibit metallic reflection. Electrolytic systems conduct the current with the accompaniment of material effects, while metallic systems conduct the current without attendant material effects of any kind. Nevertheless, the view has been gradually gaining ground that the conduction process in the two systems is similar in that conduction is effected by the motion of charged particles. While we possess a more or less comprehensive theory of the mechanism whereby the transfer of the charge is affected in electrolytic systems, a similar theory does not exist for metallic systems. Such knowledge as we do possess regarding the existence of charged particles in metals is founded chiefly on observations on the properties of metals other than those relating immediately to the conduction process. There exists little direct evidence showing that the passage of the current through the metals is effected by the motion of charged particles.

The great difficulty in the way of a direct attack on the problem of metallic conduction lies in the absence of material effects accompanying the passage of the current. In addition, there has been a complete lack of systems exhibiting properties intermediate between those of metallic and electrolytic conductors. Conducting systems fall sharply into one of two classes; namely, metallic and electrolytic conductors. In recent years, however, a class of solutions has been subjected to investigation which appears to bridge the gap between metallic and electrolytic conductors; in other words, which exhibits properties, on the one hand, in

common with those of metallic systems and, on the other hand, with those of electrolytic systems.[1] These are solutions of the alkali metals and the metals of the alkaline earth in liquid ammonia and organic derivatives of ammonia. In order to make clear the bearing of these solutions on the problem of metallic conduction, it will be necessary to discuss in some detail the properties of these solutions of the metals in liquid ammonia.

2. *Nature of the Solutions of the Metals in Ammonia.* The alkali metals are extremely soluble in liquid ammonia, yielding solutions whose external appearance depends upon their concentration. Dilute solutions of the alkali metals, as well as of metals of the alkaline earths, exhibit a fine blue color, whose absorption for all wave lengths is relatively great.[1a] At higher concentrations, the solutions possess a marked reflecting power for all wave lengths. Very concentrated solutions exhibit distinct metallic reflection of a color intermediate between that of copper and gold. Among the earlier investigators of these solutions there was much discussion as to whether the metal exists in solution as such or as a compound with the solvent. Cady[2] showed that these solutions are excellent conductors of the electric current and that in concentrated solutions the passage of the current is characterized by the absence of polarization effects at the electrodes. Finally, it has been shown that, in the case of the alkali metals, stable compounds between the metals and the solvent cannot be separated from these solutions.[3] While compounds between the metal and the solvent may exist in solution, such compounds, if they exist, possess little stability as follows from the low value of the energy changes accompanying the process of solution. In the case of the metals of the alkaline earths, however, it has been shown that compounds may be separated from solution, in which the metal is combined with ammonia. Kraus has prepared the compound $Ca(NH_3)_6$ and recently Biltz[4] has prepared the compounds $Ba(NH_3)_6$ and $Sr(NH_3)_6$. These compounds possess a metallic appearance, resembling that of the concentrated solutions of the metals in ammonia.

Kraus has determined the vapor pressure of solutions of sodium in liquid ammonia, from which he calculated the molecular weight of the metal in these solutions. Since the molecular weight can be determined only in dilute solutions, where the properties of the system are approaching those of an ideal system, it follows that molecular weight determina-

[1] Kraus, *J. Am. Chem. Soc. 29*, 1557 (1907) ; *ibid., 30*, 653, 1157 and 1323 (1908) ; *ibid., 36*, 864 (1914) ; *ibid., 43*, 749 (1921).
[1a] Gibson and Argo, *J. Am. Chem. Soc. 40*, 1327 (1918).
[2] Cady, *J. Phys. Chem. 1*, 707 (1897).
[3] Kraus, *J. Am. Chem. Soc. 30*, 653 (1908).
[4] Biltz, *Ztschr. f. Electroch. 26*, 374 (1920).

tions are always more or less in doubt. However, if the molecular weights are determined at a series of concentrations, it is possible to draw an inference as to the limit approached, as the concentration of the solution decreases, from the manner in which the apparent molecular weight varies as a function of the concentration. In the following table are given values of the apparent molecular weight of sodium dissolved in liquid ammonia at different concentrations, and in Figure 63 are shown these values plotted as ordinates against the logarithms of the concentrations as abscissas.

TABLE CXLVIII.

APPARENT MOLECULAR WEIGHT OF SODIUM IN AMMONIA AT DIFFERENT CONCENTRATIONS.

C	Apparent Mol. Wt.	*C*	Apparent Mol. Wt.
2.903	32.23	0.3665	25.31
1.841	30.70	0.3587	25.27
1.220	29.06	0.2669	23.53
0.9910	28.80	0.2516	23.43
0.9038	28.46	0.2261	23.41
0.5614	26.39	0.1565	21.62
0.5558	26.47	0.1519	21.58
0.4104	25.36		

It will be seen that, as the concentration decreases, the calculated value of the molecular weight decreases very nearly as a linear function of the logarithm of the concentration over the ranges of concentration investigated. It is not possible to state what value the molecular weight approaches as a limit, but it is evident that the limit approached has a value less than 23, the atomic weight of sodium. It appears, therefore, that sodium dissolved in liquid ammonia exists in an atomic condition and it is probable that the limit, which the molecular weight approaches, has a value less than the atomic weight of sodium. This indicates the presence of a molecular species other than the sodium atom in these solutions. While similar molecular weight determinations have not been carried out in solutions of metals other than sodium, nevertheless, in view of the similarity of the properties of solutions of the different metals in ammonia, it is highly probable that the state of these metals differs little from that of sodium.

3. *Material Effects Accompanying the Current.* The criterion for determining whether a given substance is a metallic or an electrolytic conductor is the absence or existence of material effects accompanying the passage of the current. In dilute solutions of the metals in liquid

ammonia, it has been definitely established that material effects accompany the current through these solutions. The existence of such effects is readily observed as a consequence of the characteristic color of these solutions. If a current is passed between two platinum electrodes in dilute solution of sodium or potassium in liquid ammonia, it is found that the color in the immediate neighborhood of the cathode is intensified. This result is obviously due to the fact that, as the current passes through the solution, the metallic element as an ion, either simple or complex, is carried up to the cathode. The electrolytic character of the

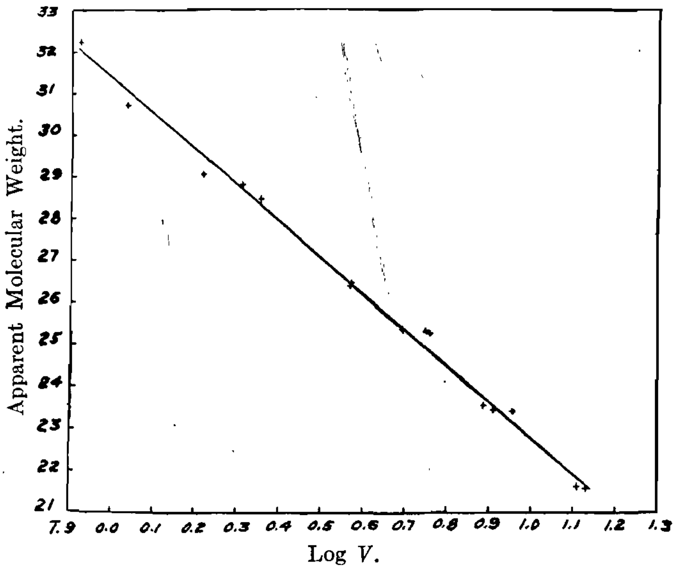

FIG. 63. Apparent Molecular Weight of Sodium in Liquid Ammonia at Different Concentrations.

conduction process in dilute solutions of these metals in liquid ammonia is therefore established; the metal is associated with the positive ion. Taking into consideration the great tendency of the alkali metals to act as positive ions, it is probable that in these solutions the metals are present, in part at least, as charged atoms which do not differ from the positive ions of salts of the same metals dissolved in the same solvent.

If positive ions are present in these solutions, then, obviously, negative ions must be present likewise. So far as may be observed, when a current passes through a solution of a metal dissolved in liquid ammonia, no material effect occurs at the anode, save that the concentration of the metal in the immediate neighborhood of this electrode is diminished.

In dilute solutions, this effect is very pronounced and, in the immediate neighborhood of the anode, the solvent appears to be completely freed from the metal, since the solution becomes colorless and transparent. No reaction of any kind appears to take place at the anode surface, no gas is evolved, nor is any manner of deposit observable. On subjecting a solution of sodium in ammonia contained in a U-shaped tube to extended electrolysis, the metal may be completely removed from the anode limb and transferred to the immediate neighborhood of the cathode surface. In this, no actual loss of the metal occurs, since on reversing the current, or on mixing the solution by shaking, the original solution is reproduced. Apparently, therefore, there is present in these solutions a negative carrier whose passage into the anode leaves behind it no observable material effect. The nature of the phenomenon is not appreciably altered if another metal is employed in place of sodium.

We commonly associate the characteristic metallic properties of a substance with the atoms of this substance; and, in the case of compounds, we associate metallic properties with the electropositive constituent. A brief consideration, however, will serve to show that this conception is erroneous, and that the electropositive constituent of a compound is entirely nonmetallic in its character. The metals owe their characteristic metallic properties, not to the electropositive constituent present, but, rather, to a common electronegative constituent. If a solution of potassium in liquid ammonia, which has a characteristic color, is placed between two solutions of potassium amide, which are transparent, then, on passing a current through this system of solutions, the motion of the color indicates the direction in which the free metal is transported under the action of the current. If the characteristic properties of a solution of potassium in ammonia were due primarily to the presence of an electropositive constituent, then we should expect that the color would move toward the cathode. It has been found, however, that, actually, under these conditions, the color moves toward the anode. As has been shown, potassium in liquid ammonia solutions is associated with the cation and moves toward the cathode. It follows that the transfer of the free metal in the solution, placed between the two solutions of potassium amide, is effected by means of the negative carrier. In passing a current through a system of the type described above, there is no indication that anything takes place as the positive ions pass from the potassium solution into the solution of potassium amide, save that the color boundary gradually moves in a direction opposite to that of the positive current, that is, toward the anode. It is probable, therefore, that the positive ion in a solution of metallic potassium in liquid

ammonia is identical with the positive ion of a solution of potassium amide in this solvent. In other words, there is present in a solution of metallic potassium a positive carrier identical with the positive carrier in potassium amide.

The positive carrier, then, in a solution of a metal in liquid ammonia, is nothing other than the normal ion of this metal and its properties in the metal solution differ in no wise from its properties in a solution of its salts. On the other hand, it is evident that, as the negative carrier moves toward the anode from the potassium solution to the potassium amide solution, free metallic potassium, that is, metallic potassium not chemically combined, is carried in the direction of the negative current toward the anode. The metallic properties of the solutions of the alkali metals in ammonia, therefore, must be due, primarily, to the negative carrier, and since free metallic potassium is present in that portion of the solution where blue color is present, it follows that this metal is generated by interaction between the potassium ion of the potassium amide solution and the negative carrier present in the solution of metallic potassium which, under the action of the potential gradient, moves into the potassium amide solution. This negative carrier, which in all likelihood is identical with the negative electron, is the essential metallic constituent of metallic substances.

There evidently exists in a metal solution an equilibrium of the type

$$M^+ + e^- = Me,$$

where M^+ is the metallic ion, e^- is the negative ion (negative electron) and Me is the neutral metallic atom. In the amide solution, as is well known, there exists an equilibrium according to the equation:

$$M^+ + NH_2^- = MNH_2.$$

It is evident that, as the negative carrier e^- is carried into the metal amide solution, equilibrium establishes itself between this carrier and the other molecular species present. In other words, the reaction takes place:

$$M^+ + e^- = Me.$$

The total amount of free metal in the solution at any time is $e^- + Me$. To what extent the metal atoms are ionized into normal positive ions and negative electrons will appear below.

4. *The Relative Speed of the Carriers in Metal Solutions.* If the conduction process in metals consists essentially in a transfer of charge due to the motion of the negative carriers, since no material effects are observable at the boundaries between different metallic conductors, it

follows that the negative carrier in all metals is the same. If this is true, and if the negative carrier in the solutions of the alkali metals in ammonia is the negative electron, then those properties of these solutions which depend upon the negative carrier should be the same in solutions of different metals. In how far this is true we shall see presently, since many of the properties of these solutions have been analyzed in terms of their ionic constituents.

Since the solutions of the metals in ammonia are ionized, the problem of determining the nature of the conduction process may be attacked in a manner similar to that employed in the case of ordinary electrolytic solutions. It is possible, in the first place, to determine the relative amount of the current carried by the two ions under given conditions. For this purpose, transference measurements might be carried out, the concentration changes resulting when a given quantity of electricity passes through the solution being determined. This experiment is difficult of execution, and consequently recourse has been had to another method, the results of which, although they are not as conclusive as direct transference determinations, nevertheless make it possible to determine the general order of magnitude of the quantities involved. The electromotive force of a concentration cell with liquid junction is given by the equation:

$$E = \frac{2nRT}{F} \log \frac{C_1\gamma_1}{C_2\gamma_2},$$

from which the value of n, the transference number, may be determined, if the electromotive force E and the concentrations $C_1\gamma_1$ and $C_2\gamma_2$ are known and if the laws of dilute solutions are applicable. Judging by the results obtained in solutions of ordinary electrolytes, this equation yields results which are approximately correct. In the case of a concentration cell which consists of two platinum electrodes placed in metal solutions, having concentrations C_1 and C_2, the work is due to the transfer of n mols of sodium per equivalent of electricity from the concentration C_1 to the lower concentration C_2. The cell is similar to that of a salt solution with reversible anodes. n is obviously the fraction of the current transported by the positive carrier in the solutions.

In Table CXLIX are given values of the electromotive force of concentration cells at different concentrations—the ratio of the concentrations of the two solutions was approximately 1:2—together with the transference number n of the cation and the ratio $\frac{1-n}{n}$.

TABLE CXLIX.

E.M.F. OF CONCENTRATION CELLS AND VALUES OF n AND $\frac{1-n}{n}$ FOR SOLUTIONS OF Na IN NH_3.

C_a	$E \times 10^3$	n	$\frac{1-n}{n}$
0.870	0.080	0.00359	277.6
0.732	0.328	0.0109	90.6
0.335	0.620	0.0231	41.2
0.164	0.72	0.0291	33.4
0.081	0.86	0.0336	28.8
0.040	1.07	0.0385	25.0
0.020	1.38	0.0575	16.4
0.010	1.80	0.0704	13.2
0.005	2.60	0.0980	9.2
0.0024	3.40	0.125	7.0

In Figure 64 are shown values of the ratio $\frac{1-n}{n}$; in other words, the ratio of the charge transported by the negative carrier to that transported by the positive carrier. On examining the table, it will be seen that, for a given concentration ratio, the electromotive force increases as the concentration decreases. At higher concentrations, the electromotive force decreases very rapidly with increasing concentration and ultimately becomes extremely small. Referring to the figure, it is seen that at low concentrations the ratio of the carrying capacities of the two ions approaches a limiting value; that of the negative carrier being approximately seven times that of the positive carrier. As the concentration increases, the relative amount of current carried by the negative carrier increases, at first slowly and then more and more rapidly. In the neighborhood of normal concentration, the current carried by the negative carrier is several hundred times as great as that carried by the positive carrier. As we have seen, the positive carrier in a sodium solution is in all likelihood identical with the positive ion of a sodium salt. As Franklin and Cady have shown, the speed of this ion varies only little with concentration. The increased carrying capacity of the negative ion at higher concentrations must, then, be due to an increase in the mean speed of the negative carriers.

It is a noteworthy fact that the carrying capacity of the negative carrier in dilute solutions is much greater than that of the sodium ion. The speed of the negative carriers in these solutions must therefore be much greater than that of the sodium ion. The speeds of the different

ions of salts in ammonia solution, as we have seen, do not differ greatly. This indicates that the negative carrier in the metal solutions is of relatively small dimensions. Nevertheless, if the negative carrier in these solutions were the negative electron unassociated with matter, we should expect a much greater value. It is known, however, that, owing to electrostatic action, a charge placed in a fluid medium tends to condense about it an atmosphere of the surrounding molecules. In gases at higher pressures, the speed of the negative carrier is as low as, and often lower

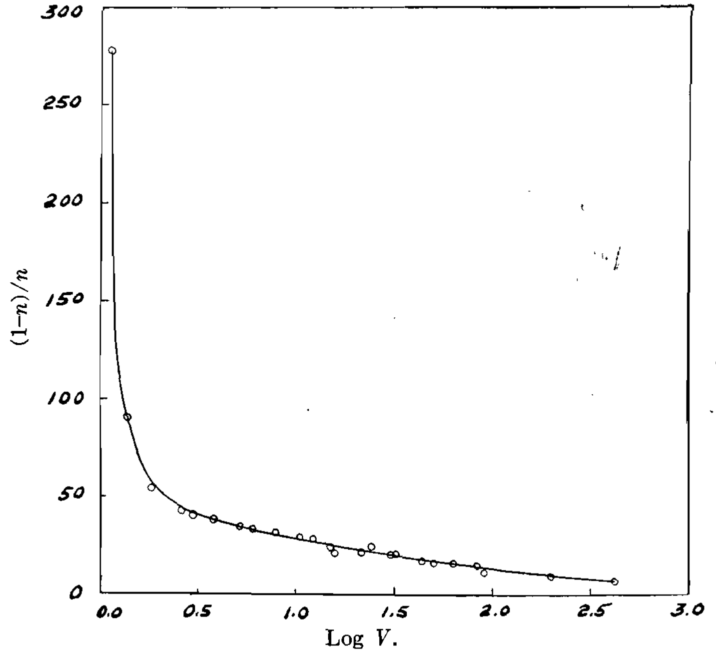

FIG. 64. Relative Speed of the Negative and Positive Ions of Sodium in Liquid Ammonia at Different Concentrations.

than, that of the positive carrier and it is only at low pressures that the negative carrier in gases loses its envelope of surrounding molecules and acquires a high speed. It is not surprising, therefore, that the negative electron in liquid ammonia should possess a speed comparable with that of ordinary ions. At higher concentrations, however, as is indicated by the increased carrying capacity of the negative ion, the size of the surrounding envelope evidently diminishes and, indeed, it has been shown that some of the negative carriers are completely unassociated with ammonia.

If the negative carriers are associated with ammonia, then obviously,

due to the motion of this carrier, ammonia will be carried from the dilute to the concentrated solution. If the vapor pressures of the two solutions are known, we may calculate the work due to the transfer of solvent by the negative carrier, the number of molecules of ammonia associated with this carrier being assumed. The complete expression for the electromotive force is:

$$E = \frac{2nRT}{F} \log \frac{M_1^+}{M_2^+} + m(1 - n) \frac{RT}{F} \log \frac{p_1}{p_2},$$

where m is the number of molecules of ammonia associated with the negative carrier and p_2 and p_1 are the vapor pressures of the two solutions. If we place $n = 0$ in this equation, that is, if we assume that all the current is carried by the negative carriers, we may calculate a maximum value for m, if the electromotive force of the cell and the vapor pressures of the solutions are known. For a concentration cell between solutions whose concentrations were 1.014 and 0.627 normal, the measured electromotive force was 0.08×10^{-3} volts, and the ratio of the vapor pressures was 1/1.006. This yields for m the value 0.67; that is, a value less than unity. Since m cannot be less than unity, it follows that at least a portion of the current must be carried by carriers not associated with ammonia. It is evident, from the manner in which the electromotive force and the vapor pressure of ammonia solutions vary with the concentration, that at higher concentrations the value calculated for m would be even smaller. The negative carriers in solution, therefore, consist of negative electrons surrounded with ammonia molecules. As the concentration of the solution increases, the number of ammonia molecules associated with the carriers decreases and ultimately a portion of the carriers becomes entirely free from ammonia molecules. The great increase in the relative carrying capacity of the negative carriers at higher concentrations is due to the presence of these free negative electrons.

5. *Conductance of Metal Solutions.* If the increased carrying capacity of the negative carrier is, in fact, due to an increase in the mean speed of this carrier, the speed of the positive carrier remaining substantially constant, then the equivalent conductance of solutions of the metals in liquid ammonia should increase largely with the concentration at higher concentrations. Since the determinations of the molecular weight, as well as the results on the motion of the boundary between a metal and a metal amide solution, indicate that an equilibrium exists between the positive ions and the negative carriers and the neutral atoms, it is to be expected that the ionization of the metal will vary as a

function of the concentration. According to these views the state of a metal dissolved in ammonia does not differ materially from that of a salt of the same metal dissolved in this solvent. The only material difference lies in the fact that, whereas in the metal solution the negative electron functions as negative carrier, in the salt solution, a negative ion, that is, a negative electron attached to an atomic complex, serves as negative carrier. We should therefore expect the equivalent conductance in dilute solutions to vary as a function of the concentration in a manner similar to that of normal electrolytes. In other words, with decreasing concentration of the solution, the equivalent conductance should increase and approach a limiting value.

In Table CL are given values of the equivalent conductance of solutions of sodium in liquid ammonia at its boiling point at different concentrations. The density of the solutions not being known, the dilutions given under the column headed V represent the number of liters of pure ammonia of density 0.674, in which one atom of sodium is dissolved. In the more concentrated solutions the density is considerably lower than that of pure ammonia.

TABLE CL.

CONDUCTANCE OF SODIUM IN AMMONIA AT — 33.5°.[5]

V	Λ	V	Λ
0.5047	82490.	13.86	478.3
0.6005	44100.	30.40	478.5
0.6941	23350.	65.60	540.3
0.7861	12350.	146.0	650.3
0.8778	7224.	318.6	773.4
0.9570	4700.	690.1	869.4
1.038	3228.	1551.0	956.6
1.239	2017.	3479.0	988.6
2.798	749.4	7651.0	1009.0
6.305	554.7	17260.0	1016.0
		37880.0	1034.0

In Figure 65 the upper curve represents the equivalent conductance as a function of log V up to a concentration of approximately normal. From an inspection of the table and the accompanying figure, it will be seen that the conductance curve exhibits a minimum in the neighborhood of 0.05 N. At lower concentrations the equivalent conductance increases as the concentration decreases and approaches a limiting value in the neighborhood of 1016. The form of the curve at these concentrations is

[5] Kraus, *loc. cit.*

similar to that of binary electrolytes in liquid ammonia, the only material difference being that the conductance has a much higher value. The equivalent conductance of the sodium ion is 130. It follows, then, that the equivalent conductance of the negative carrier in these solutions at low concentrations is in the neighborhood of 886, or 6.8 times that of the sodium ion. We saw in the previous section that the results of measurements of the electromotive force of concentration cells indicate that the carrying capacity of the negative carrier is approximately 7 times that of the positive ion in a sodium solution. This value, therefore, is in excellent agreement with the value 6.8 obtained from conductance

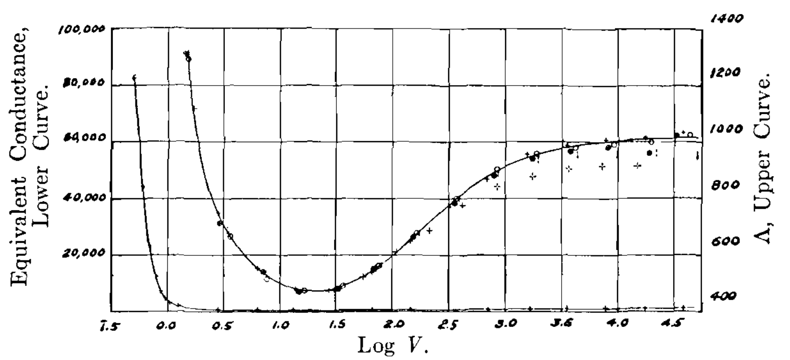

FIG. 65. Equivalent Conductance of Sodium in Liquid Ammonia at —33.5° at Different Concentrations.

measurements. Evidence has already been presented which indicates that the positive ion in a sodium solution is identical with the positive ion in a solution of a sodium salt. The fact that the conductance of the positive ion, as derived from measurements with the metal solutions, corresponds with that of the sodium ion as derived from measurements with solutions of sodium salts confirms this hypothesis. The positive ion in a solution of sodium in liquid ammonia is therefore the normal sodium ion.

If, now, we examine the conductance curve in the more concentrated solutions, we see that below a concentration of 0.05 N the conductance increases with the concentration, the increase being the greater the higher the concentration. This, again, confirms the conclusion derived from a study of the electromotive force of concentration cells. As the concentration increases, the relative carrying capacity of the negative carrier increases. The increase in conductance is due to an increase in the mean speed of this carrier, since at higher concentrations the con-

ductance increases enormously, which result may be accounted for only on the assumption that the speed of one or both of the carriers increases. Since one of these carriers is the normal sodium ion, it follows that the conductance is due to an increase in the speed of the negative carrier. If these conclusions are valid, then, at high concentrations, the conductance of the metal solutions should approach that of the metals themselves, for at high concentrations the number of carriers and negative electrons present in the solution becomes comparable with that of the total number of molecules present, in which case we should expect that a considerable fraction of these carriers would be free from ammonia molecules. This is borne out by the results of conductance measurements. As may be seen from Table CL, the equivalent conductance increases from a value of approximately 475 at a concentration of 0.05 N to a value of approximately 2000 at normal and to approximately 82000 at a concentration of 2 normal. At this concentration the specific conductance of the solution is 163.5, the specific conductance of mercury being 1.063×10^4, which is about six times that of the metal solution at the concentration in question. The lower curve in Figure 65 shows how the conductance varies with concentration up to 2 N.

In the following table are given values of the specific conductance of solutions of sodium in liquid ammonia up to the saturation point of these solutions.[6]

TABLE CLI.

SPECIFIC CONDUCTANCE OF CONCENTRATED SOLUTIONS OF SODIUM IN AMMONIA AT —33.5°.

V	μ	V	μ
0.1081	5047.0	0.5099	148.3
0.1331	4954.0	0.7612	20.21
0.1804	2687.0	0.9265	5.988
0.2768	1070.0	1.298	1.269
0.3230	714.0	1.674	0.6465

The results for sodium, together with those for potassium, are shown graphically in Figure 66, where the logarithms of the specific conductance are plotted against the logarithms of the dilution V as defined above. The curve passing through the points is that of potassium; the other, that of sodium. At the highest concentrations, the solutions were saturated, so that the specific conductance was independent of the total amount of ammonia present. The second point for the value $V = 0.1331$

[6] Kraus and Lucasse, *J. Am. Chem. Soc.* *43* (Dec., 1921).

lies just below the saturation point. The specific conductance of the saturated solution is 0.5047×10^4; or, almost precisely one half that of mercury at 0°. That the solutions of the metals in liquid ammonia at these concentrations are metallic admits of no doubt. They exhibit all the properties of metallic substances, both optical and electrical. A brief consideration will show, indeed, that in these solutions the metal possesses an exceptionally high conducting power compared with that of

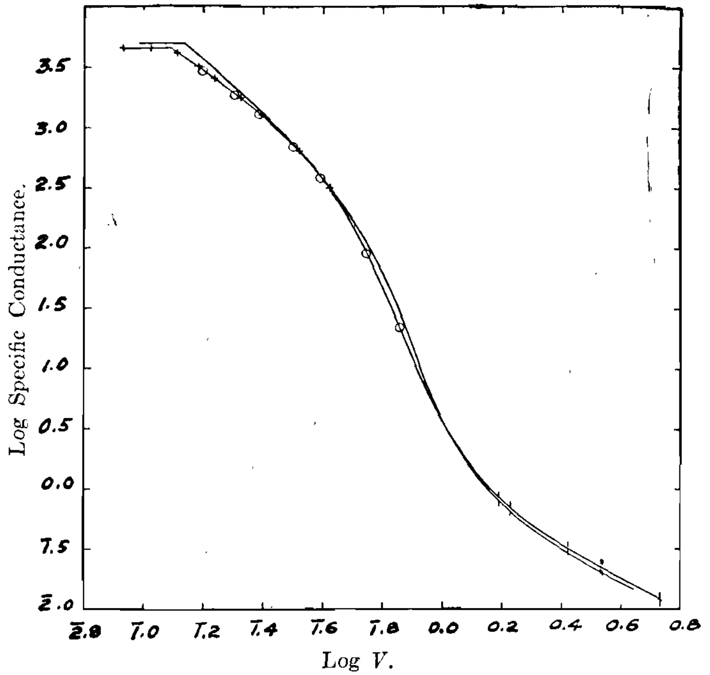

FIG. 66. Conductance of Concentrated Solutions of Sodium and Potassium in Liquid Ammonia at —33.5°.

many metals. Obviously, if metallic conduction is due to the motion of charged carriers, then two factors influence the conductance; in the first place, the resistance which the carriers experience in their motion, and, in the second, the number of carriers present in a given volume. In comparing the conducting power of different metals, it is not sufficient to merely compare their specific conductances. The concentration factor should also be taken into account. If the specific conductance is divided by the number of gram atoms per cubic centimeter, the ratio yields the atomic conductance of the metal. The atomic conductance of a satu-

rated solution of sodium in ammonia[6a] is 1.1×10^6 The atomic conductance of metallic sodium at room temperatures is 5.05×10^6. The conductance of the saturated solution is therefore comparable with that of the pure metal. Values of the atomic conductance of other metals will be found in Table CLIII of the next chapter. The atomic conductance of sodium solutions is about the same as that of osmium and tin and much greater than that of mercury (liquid) and bismuth.

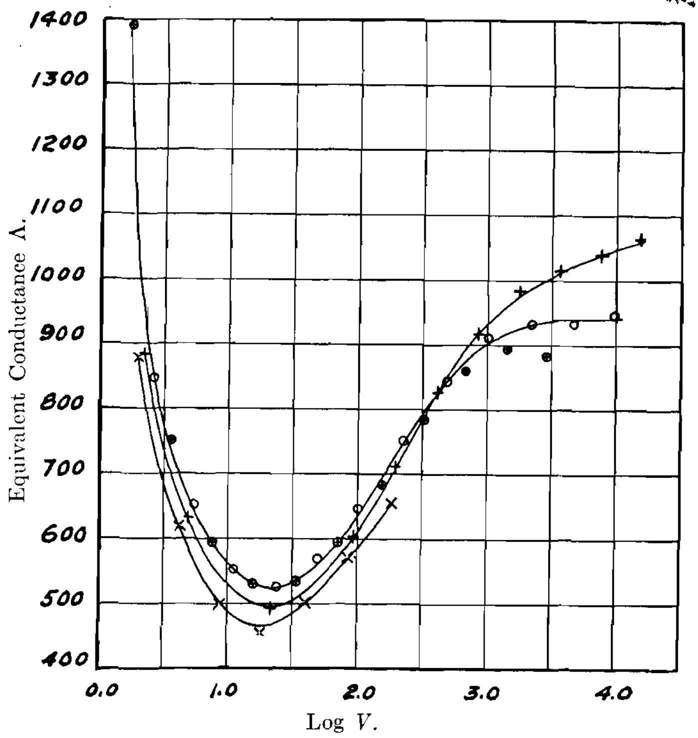

FIG. 67. Conductance of Dilute Solutions of Potassium and Lithium and of Mixtures of Sodium and Potassium in Liquid Ammonia at —33.5°.

The view was expressed, above, that the negative carrier for different metals dissolved in liquid ammonia is the same and is, in fact, the negative electron, which carrier presumably effects the passage of the current through all metallic substances. If this view is correct, then, at higher concentrations, where the conductance of the solution is due almost entirely to the negative electron, solutions of different metals in ammonia should exhibit very nearly the same properties. It is to be

[6a] This is based on the value 0.54 for the density of the saturated solution as determined approximately by Dr. Lucasse in the Author's Laboratory. This value may be in error by several per cent.

expected, of course, that minor variations will be observed, since equivalent solutions are not physically identical. The densities of potassium and sodium solutions, for example, differ; and the amount of ammonia associated with the positive ions in these solutions doubtless differs. Aside from minor differences, we should expect those properties of metal solutions, which depend upon the negative carrier, to be relatively independent of the nature of the metal. In Figure 67 are shown the conductance curves of dilute solutions of potassium, lithium, and mixtures of sodium and potassium. The uppermost curve is that of potassium, the lowest that of lithium, while the intermediate curve is that of a mixture of sodium and potassium. The curve for mixtures of sodium and potassium lies intermediate between that of sodium and of potassium. It is seen that in the case of very dilute solutions of potassium and lithium, the conductance values, as shown, lie below the true values owing to the fact that these metals react with the solvent according to the equation:

$$Me + NH_3 = MeNH_2 + \tfrac{1}{2}H_2;$$

that is, the metals react with the solvent to form the amides. This removes a portion of the metal from solution and consequently the conductance values measured are lower than the true values. From the extensive data presented by Kraus, however, there can be no doubt as to the cause for the low values observed in dilute solutions in the case of potassium and lithium. At intermediate concentrations, where the formation of amide is not marked, the conductance of the solutions diminishes in the order: potassium, sodium, lithium. At a given concentration, the difference in the values of the conductance of these metals corresponds approximately to the difference in the conductance of the positive ions of these metals. This shows that in dilute solutions of potassium, sodium and lithium in liquid ammonia, the conductance of the negative carrier is the same; presumably, therefore, the negative carriers are identical in the three cases. At higher concentrations, where the conductance of the positive ion becomes negligible in comparison with that of the negative carrier, we should expect the specific conductance of the solutions to be practically the same at the same equivalent concentration. As may be seen from Figure 66, the conductance curves for sodium and potassium possess the same form, and over a considerable range of concentration they are practically identical.[7] At higher concentrations, slight variations occur as might be expected, since the densities of these solutions are not the same. The conclusion that the

[7] Kraus and Lucasse, *loc. cit.*

negative carrier of the different metals is the same appears, therefore, amply justified.

The temperature coefficient of sodium solutions in liquid ammonia has been measured. In Table CLII are given values of the resistance of fairly dilute sodium solutions from the boiling point of liquid ammonia up to 85°C. In the last column are given values of the mean percentage temperature coefficient of these solutions over various temperature intervals referred to the resistance at —33°.[7a]

TABLE CLII.

Temperature Coefficient of Dilute Sodium Solutions.

t	R	$\frac{\Delta(1/R)}{\Delta t(1/R)_{33}} \times 100$
—33°	124.3	..
—13°	85.7	2.25
+17°	43.4	4.69
+48°	28.2	5.34
+85°	15.6	9.00

It is seen that at low temperatures the temperature coefficient of the conductance of these solutions is approximately 2 per cent, and as the temperature increases the temperature coefficient increases markedly reaching a value of 9 per cent for the interval between 45° and 85°. This behavior of the metal solutions in liquid ammonia is in striking contrast to that of normal electrolytes dissolved in this solvent. At ordinary concentrations, the conductance of these solutions passes through a maximum in the neighborhood of room temperatures, the conductance decreasing with increasing temperatures above this point. It is obvious that the factors involved in the temperature coefficients of the metal solutions are very different from those involved in solutions of ordinary electrolytes. It is difficult, in the present state of our knowledge, to state to what the high value of the temperature coefficient is due. However, since in fairly dilute solutions the conductance is due primarily to the negative electron more or less associated with ammonia, it is possible that the high value of the temperature coefficient at higher temperatures is due to an increase in the mean speed of the negative carriers as a result of a diminution in the size of the solvent envelope with which the negative electrons are surrounded.

While at low concentrations the temperature coefficient of the metal

[7a] Kraus, *loc. cit.*

solutions is greater than that of ordinary electrolytes, at high concentrations the temperature coefficient is markedly lower.[8] At a dilution $V = 0.18$, the temperature coefficient is approximately 0.17%. It is evident that at higher concentrations the value of the temperature coefficient decreases as the concentration increases. In the neighborhood of the saturation point, the coefficient is not far from zero, and, were it possible to prepare solutions having higher concentrations, it might be expected that the temperature coefficient would even become negative as it is in metals.[8a]

These data on the temperature coefficient of the metal solutions in liquid ammonia serve further to differentiate these solutions from solutions of ordinary electrolytes. The behavior of the very concentrated solutions clearly indicates an intimate relation between these solutions and ordinary metallic conductors. The properties of the metal solutions in liquid ammonia, therefore, supply abundant evidence to the effect that conduction in metals is due to the motion of a negative carrier of sub-atomic dimensions, which carrier is the same for all metals. Since the only carrier of sub-atomic dimensions which has been observed is the negative electron, we may infer that the effective carrier in metals, as in these solutions, is the negative electron.

[8] Observations by Dr. W. W. Lucasse in the Author's Laboratory.

[8a] Since this was written, the temperature coefficient of sodium in liquid ammonia has been determined by Dr. Lucasse from a dilution $V = 1.7$ up to the saturation point. The coefficient for the saturated solution is 0.067%. As the concentration decreases, the temperature coefficient increases decidedly reaching a maximum of 3.65% at $V = 1.06$ after which it decreases more slowly, falling to 2.47% at $V = 1.7$.

Chapter XV.

The Properties of Metallic Substances.

1. *The Metallic State.* With the exception of the elements of the argon group and the strongly electronegative elements of lower atomic weight, elementary substances are metallic. Compounds between strongly electronegative and strongly electropositive elements, as well as compounds between the more electronegative elements, are non-metallic; while compounds between distinctly metallic elements are throughout metallic. Compounds between the less strongly electronegative elements and the less strongly electropositive elements are often metallic in the solid state. Thus the compounds of the alkali metals and the metals of the alkaline earths with the elements of the halogen and of the oxygen groups are non-metallic; while compounds of the less electropositive elements, such as lead and iron, with the elements of the oxygen group are often metallic. Within this class are also included certain free electropositive groups, containing both metallic and non-metallic elements, and possibly groups containing only nonmetallic elements. Thus, the free group CH_3Hg is metallic,[1] while certain of the substituted ammonium groups form stable metallic amalgams.[2] There is also evidence that the quaternary substituted ammonium groups are soluble in ammonia in the free state, and that in solution their properties resemble those of the alkali metals.[3] The property of metallicity, therefore, is not to be looked upon as an atomic property, since various groups of nonmetallic elements in the free state exhibit metallic properties.

The metals thus comprise a major portion of the elementary substances and a large number of compounds between metallic and non-metallic elements. While nonmetallic compounds may, in a large measure, be accounted for through the interaction of the negative electrons with atoms, a similar theory of the constitution of metallic compounds has not thus far been developed. One of the remarkable facts

[1] Kraus, *J. Am. Chem. Soc.* *35*, 1732 (1913).
[2] McCoy and Moore, *J. Am. Chem. Soc.* *33*, 273 (1911).
[3] Palmaer, *Ztschr. f. Elektroch.* *8*, 729 (1902) ; Kraus, *loc. cit.*

in connection with inter-metallic compounds is the large number of compounds derivable from a single pair of elementary substances. The constitution of these compounds does not harmonize well with our present conceptions of valence. The study of these substances is attended with many experimental difficulties and their nature at the present time is little understood.

Metallic substances are characterized by certain well-defined properties, chiefly electrical and optical, which are common to all.[4] This community of property among metallic substances indicates some common element within their constitution. During the past few decades the view has been gaining ground that the properties of metallic substances are primarily due to the presence of charged particles, presumably negative electrons, which are relatively free to move within the body of the metal. While this theory of the constitution of metals is in good agreement with observed facts from a qualitative point of view, it has not been found possible to elaborate a detailed theory of metallic substances which accounts successfully for the major portion of their characteristic properties.

2. *The Conduction Process in Metals.* Metallic conductors are differentiated from electrolytic conductors in that the passage of the current through them is unaccompanied by an appreciable transfer of matter. If a current is passed for an indefinite period of time through a series of metallic conductors, no material effects are observable, either within the conductors themselves or at the boundaries between them. If the conduction process in metals is due to the motion of negative electrons, then there must likewise be present in the metals positively charged constituents or ions which, conceivably, may take part in the conduction process. In all likelihood the amount of matter transferred by these carriers is extremely small, and may under ordinary conditions escape observation. Experiments carried out with amalgams of sodium and potassium indicate that in these systems an appreciable transfer of matter actually takes place.[5] Curiously enough, in these amalgams, the electropositive constituent, that is, the alkali metal, was found to be carried toward the anode and not toward the cathode as might have been expected. The data are as yet too meager to warrant drawing

[4] A very complete summary of the literature relating to metallic substances is given by J. Koenigsberger in Handbuch d. Elektrizität u. d. Magnetismus by L. Graetz, Leipzig, J. A. Barth (1920), Vol. *3*, pp. 597-724. The older literature is also summarized in Winkelmann's Handbuch d. Physik, Vol. *4*, pp. 344-384, and Baedeker's Elektrische Erscheinungen in Metallischen Leitern, Vieweg, Braunschweig (1911).

[5] Lewis, Adams and Lanman, *J. Am. Chem. Soc.* *37*, 2656 (1915).

conclusions as to the part which the positive constituent plays in metallic conduction. It appears probable, however, that in suitable metallic systems an appreciable transfer of matter accompanies the passage of the current.

The view that the conduction process in metals is an ionic one is the only one in agreement with our present notions regarding the constitution of matter. The absence of material effects accompanying the transfer of electricity indicates a common carrier in all metallic substances. The fact that no positively charged carrier of sub-atomic dimensions is known lends probability to the view that metallic conduction is due to the motion of the negative electron, the only known carrier of sub-atomic dimensions.

Direct evidence in support of the electron theory of metallic conduction is very meager. Tolman and Stewart [6] have studied the current flow induced in metallic conductors under acceleration. From their measurements, they have calculated the ratio of the effective mass of the carriers to the quantity of electricity flowing. Their results indicate that the current is due to the motion of a negative carrier, the ratio of whose mass to the charge corresponds with that of the negative electron. For copper, aluminum and silver conductors, Tolman and Stewart found for the value of $1/m$, assuming $O = 16$, the values 1660, 1590, and 1540 respectively. These are somewhat lower than corresponds to the mass of a slowly-moving negative electron, but the difference lies within the limits of experimental error. The results of investigations on the properties of solutions of the alkali metals in liquid ammonia, described in the preceding chapter, likewise furnish striking evidence in support of the electron theory of metallic conduction. Other properties of the metals, such as the Hall effect, and particularly the emission of negative electrons by metals at higher temperatures, lend support to this theory. The precise nature of the conduction process of metals, however, still remains very obscure.

3. *The Conductance of Elementary Metallic Substances.* The order of magnitude of the conductance of metals, in itself, furnishes evidence in support of the electron theory of metallic conduction. In Table CLIII are given values of the atomic conductance and the specific resistance, as well as of the mean temperature coefficient α of the resistance of a number of elementary metals.

[6] Tolman and Stewart, *Phys. Rev.* 8, 97 (1916); *ibid.*, 9, 164 (1917).

TABLE CLIII.

ATOMIC CONDUCTANCE, SPECIFIC RESISTANCE AND RESISTANCE TEMPERATURE COEFFICIENT OF ELEMENTARY METALS AT 0°.

Metal	$\Lambda \times 10^{-6}$	$\sigma_0 \times 10^6$	$\alpha_{0-100} \times 10^3$
Silver	6.999	1.468	4.10
Potassium	6.503	6.100	5.5
Sodium	5.288	4.28	5.1
Rubidium	4.845	11.60	..
Copper	4.559	1.561	4.33
Gold	4.547	2.197	3.98
Caesium	3.898	18.12	..
Aluminium	3.834	2.563	4.26
Magnesium	3.215	4.355	3.90
Chromium	2.989	4.40	..
Calcium	2.457	10.50	..
Indium	1.905	8.370	4.74
Cadmium	1.875	10.023	4.24
Rhodium	1.811	4.700	4.43
Zinc	1.713	5.751	4.17
Lithium	1.534	8.550	4.57
Iridium	1.414	8.370	3.71
Tantalum	1.339	14.60	3.47
Tin	1.252	13.048	4.47
Osmium	1.119	9.500	4.2
Thallium	0.9775	17.633	5.17
Nickel	0.9613	12.323	4.87
Lead	0.9222	20.380	4.22
Palladium	0.9082	10.219	3.77
Platinum	0.8314	11.193	3.92
Iron	0.8031	9.065	6.57
Strontium	0.7194	24.75	..
Cobalt	0.7064	9.720	3.66
Manganese	0.6561	4.400	..
Antimony	0.4658	39.00	4.73
Arsenic	0.3735	35.10	3.89
Gallium	0.2208	53.40	..
Bismuth	0.1972	108.00	4.46
Mercury	0.1564	95.80	0.88

As may be seen from the table, the specific resistance of silver is 1.47×10^{-6}. Compared with this, the specific resistance of fused salts is of the order of 1.0 and that of electrolytes, at normal concentration, 10.

In comparing the conducting power of metals it is more rational to employ the atomic, or perhaps even the equivalent, rather than the specific conductance. On this basis, metallic conductors exhibit many rela-

tionships which otherwise are not apparent.[7] The atomic conductance of potassium and of silver is of the order of 6×10^6 and that of mercury at ordinary temperatures, which is a relatively poor conductor, 1.5×10^5. Compared with these values, the equivalent conductance of fused salts is in the neighborhood of 50 and that of electrolytes at low concentrations 100. In a few instances, the equivalent conductance of electrolytes is considerably higher, as, for example, in aqueous solutions at high temperatures, where it approaches a value of 1000, and in solutions of the alkali metals in liquid ammonia at low concentrations. The above values relate to the conductance of metals at ordinary temperatures. If a similar comparison were made at lower temperatures, the relative conducting power of the metals would be found to be enormously greater. The conductance of metals at very low temperatures will be discussed in the next section.

The conductance of elementary metals in the liquid state is, in general, lower than in the solid state. The process of fusion is accompanied by a discontinuous change in the conductance values. In the following table are given the ratios of the specific conductances μ_s/μ_l of metals in the solid and liquid states, together with the ratio of their specific volumes v_l/v_s.

TABLE CLIV.

CHANGE OF THE SPECIFIC CONDUCTANCE OF ELEMENTARY METALS ON MELTING.

Metal	Melting Point	Specific Conductance at the Melting Point	μ_s/μ_l	v_l/v_s
Lithium	177.8°	2.6×10^4	2.51	..
Sodium	97.6	9.5×10^4	1.34	1.024
Potassium	62.5	7.7×10^4	1.39	1.024
Caesium	26.4	2.54×10^4	1.65	1.027
Zinc	419.	2.7×10^4	2.0	> 1
Cadmium	321.	2.9×10^4	1.96	1.047
Mercury	—38.8	1.10×10^4	4.1	1.036
Thallium	301.	1.35×10^4	2.0	..
Tin	232.	2.1×10^4	2.2	1.028
Lead	327.	1.06×10^4	1.95	1.034
Antimony	629.5	0.88×10^4	0.70	..
Bismuth	269.	0.78×10^4	0.46	0.967

[7] Richarz, *Ztschr. f. anorg. Chem.* *50*, 356 (1908); Benedicks, *Jahrb. f. Rad.* *13*, 351 (1916).

As may be seen from the table, expansion of the metal on melting is, in general, accompanied by an increase of resistance. The change in the specific conductance is particularly marked in the case of mercury. In the case of antimony and bismuth, the specific conductance increases on fusion. This is particularly marked in the case of bismuth, which expands on fusion.

A change in state of an elementary metal is at times accompanied by a discontinuous change in the conductance values and at times only by discontinuity in the temperature coefficient. The transition from gray tin to ordinary tin is doubtless accompanied by a discontinuous change in resistance, although the specific conductance of gray tin appears not to have been determined. In the case of elementary metals of very low conducting power, such as metallic silicon, discontinuous changes in the conductance curve have been observed. In other cases, as, for example, the transition of the magnetic metals at the recalescence point, the resistance curve itself is continuous, but the temperature coefficient undergoes a discontinuous change, as we shall see below.

4. *The Conductance of Elementary Metals as a Function of Temperature.* The electrical properties of different solid elementary metals are strikingly similar. With increasing temperature, the resistance of elementary metals increases, the mean coefficient having a value in the neighborhood of 0.004, which does not differ greatly from the coefficient of expansion of gases at low pressures. Certain metals, as, for example, the magnetic metals iron and nickel, have coefficients much higher than this value, particularly at higher temperatures. The resistance of most metals increases approximately as a linear function of the temperature, and over larger temperature ranges the resistance may be expressed very nearly as a function of the temperature by means of a quadratic equation.

With decreasing temperature, the resistance of pure metals decreases and, down to liquid air temperatures, it would appear that a value of zero is being approached as a limit at the absolute zero. The experiments of Kammerlingh Onnes at liquid helium temperatures, however, have brought to light the remarkable fact that at very low temperatures the resistance of pure metals undergoes a discontinuous change. When a certain temperature is reached, the resistance falls off abruptly to values which are almost negligible, if not actually zero.[8] For example, at 4.24° K. the resistance of mercury in terms of its value at 0° (extrapo-

[8] Kammerlingh Onnes, numerous papers in the Proceedings of the Koninklijke Akademie van Wetenschaften te Amsterdam. A summary of the work relating to the properties of metals at low temperatures will be found in articles by J. Clay, *Jahrbuch der Radioaktivität und Elektronik* *12*, 259 (1915); *ibid.*, *8*, 383 (1911); see also, Crommelin, *Phys. Ztschr.* *21*, 274, 300 and 331 (1920).

lated) is 0.163, while at 4.185° the resistance is less than 10^{-6}, and at 2.45° less than 2×10^{-10}. Similarly, the resistance of tin vanishes at a temperature of 3.78° K. and that of thallium at 2.3° K. The resistance of lead vanishes at a temperature between 4.3° and 20°, probably in the neighborhood of 6° K. Metals in a condition in which their resistance vanishes are said to be in a supraconducting state. Certain metals, such as platinum and copper, do not exhibit supraconductance. In such metals the conductance falls to a low limiting value, after which it remains independent of temperature. In the following table are given values for the resistance of platinum in arbitrary units, at a series of temperatures.

TABLE CLV.

RESISTANCE OF PLATINUM AT LOW TEMPERATURES.

T abs.	Resistance
273.1	1.0
20.1	0.0170
14.3	0.0136
4.3	0.0119
2.3	0.0119
1.5	0.0119

It is apparent from this table that at a temperature in the neighborhood of 4.3° absolute the resistance of platinum falls to a value a little greater than 0.01 of its value at 0°. Below this temperature, the resistance remains constant. Similar results have been obtained for other metals such as copper and iron. Apparently, those metals, which exhibit a marked tendency to form solid solutions with other metals, do not exhibit the phenomenon of supraconductance. It has been suggested that the absence of this phenomenon in these metals is due to the influence of minute traces of impurities.

The significance of the phenomenon of supraconductance is not fully understood as yet. Various theories have been proposed in explanation of this phenomenon, as, for example, that of J. J. Thomson.[9] Bridgman[10] has recently suggested that a polymorphic change takes place at the point where supraconductance intervenes. According to this view, the normal state of a substance, or of a crystal, at very low temperatures is that of supraconductance. The residual resistance found in the case of such metals as platinum is due to non-homogeneity between the surfaces of the individual crystals of which the conductor is composed. At

[9] J. J. Thomson, *Phil. Mag.* *30*, 192 (1915).
[10] Bridgman, *J. Wash. Acad.* *11*, 455.

the present time it is not possible to reach any certain conclusion as to the nature of these phenomena.

The mean temperature coefficients α for a number of elementary substances are given in Table CLIII above. In the following table are given values of the temperature coefficient $\alpha = \frac{1}{R_t}\frac{dR_t}{dt}$ for a number of metals at different temperatures.

TABLE CLVI.

TEMPERATURE COEFFICIENT $\frac{1}{R_t}\frac{dR_t}{dt}$ FOR METALS AT DIFFERENT TEMPERATURES.

Temperature	Ag	Fe	Ni	Al	Mg	Cu
25°	0.0030	0.0052	0.0043	0.0034	0.0050	0.0036
100	0.0036	0.0068	0.0043	0.0040	0.0045	0.0038
200	0.0039–	0.0090	0.0070	0.0042	0.0041	0.0040
300	0.0040	0.0111	**0.0080**	0.0043	0.0043	0.0041
400	0.0042	0.0133	0.0036	0.0046	0.0040	0.0042
500	0.0044	0.0147	0.0030	0.0050	0.0036	0.0043
600	0.0046	0.0170	0.0028	0.0060	0.0100	0.0044
700	0.0047	**0.0224**	0.0026	0.0120	0.0250	0.0047
800	0.0052	0.0120	0.0025	at 625°	at 625°	0.0053
900	0.0058–	0.0046	0.0028	..	..	0.0057
1000	..	0.0050	0.0037	..	..	0.0062
1075	..	..	0.0062	..	..	..

It will be observed, from the table, that the temperature coefficient increases with increasing temperature. The magnitude of the coefficients of different metals differs considerably, particularly those of the magnetic metals, iron and nickel. It is interesting to note that, as the transition point of these metals is approached, the temperature coefficient increases very largely. The temperatures at which the transition points are reached are indicated in the table by heavy type. Beyond the transition points, the temperature coefficients fall back to normal values, in the case of both iron and nickel. A somewhat similar phenomenon is observed in the neighborhood of the melting point, which is illustrated in the case of aluminium and magnesium, particularly in the case of the latter element. The temperature coefficient increases considerably as the melting point is approached. Beyond the melting point, the coefficients are, in general, smaller than below this temperature.

The temperature coefficients of elementary liquid metals vary within

wide limits. The coefficients are greatest for the alkali metals, in which case they differ very little from those of the solids. In other cases, the temperature coefficients reach extremely small values, as, for example, in that of zinc. As a rule, the temperature coefficients of liquid metals have values in the neighborhood of one fifth that of the solid metals. In the following table are given the mean temperature coefficients of a number of liquid metals referred to their resistance at the lowest temperature given.

TABLE CLVII.

TEMPERATURE COEFFICIENT OF LIQUID METALS.

Metal	α	Temperature Interval
Sodium	38.5×10^{-4}	M.P.
Potassium	41.8×10^{-4}	"
Lithium	27.3×10^{-4}	178–230
Tin	5.9×10^{-4}	M.P.–350
Bismuth	4.1×10^{-4}	"
Thallium	3.5×10^{-4}	"
Cadmium	1.3×10^{-4}	"
Lead	5.2×10^{-4}	"
Copper	4.12×10^{-4}	1084–1500
Aluminium	5.42×10^{-4}	653–1250
Iron	3.66×10^{-4}	1055–1650
Nickel	1.67×10^{-4}	1451–1650
Zinc	0.3×10^{-4}	419–500
Tin	4.68×10^{-4}	232–1600
Cadmium	2.26×10^{-4}	500–650
Antimony	1.37×10^{-4}	631–800

The temperature coefficients here given cannot be directly compared with those of the solid metals at ordinary temperatures, since the coefficients are referred to the resistance of these metals at higher temperatures. In a number of instances values have been extrapolated to ordinary temperatures, in which case the coefficients are invariably smaller than those of solid metals. For example, the values for copper, aluminium and iron are 7.45×10^{-4}, 8.40×10^{-4} and 8.15×10^{-4}, respectively.

The temperature coefficient as commonly measured is the resultant effect of temperature change and volume change. The temperature coefficient at constant volume differs materially from that at constant pressure, depending upon the influence of pressure upon the resistance of the conductor in question. In solid metals, the pressure effect is relatively

small, while the resistance-temperature coefficient is large; consequently, the temperature coefficient is not greatly affected by the volume change. In liquid metals, however, where the temperature coefficient is small and the resistance pressure coefficient relatively large, the volume change has a material influence on the observed temperature coefficient. In the case of mercury,[11] the resistance temperature coefficient $\left(\frac{1}{R}\right)\left(\frac{dR}{dt}\right)_V = -6.9\times10^{-4}$ as against the value of $+8.9\times10^{-4}$ for the resistance-temperature coefficient at constant pressure. It is a significant fact that the resistance of a liquid metal at constant volume should decrease with increasing temperature. In this connection it may be noted that Somerville[12] found that zinc wire, wrapped in the form of a spiral around a silica tube, exhibited a marked negative temperature coefficient above the melting point, the resistance varying very nearly as a linear function of the temperature. In this case the metal in the fluid state was held together by surface forces. The temperature coefficient of molten zinc in a quartz tube was found to be positive but of a very low value.

5. *The Conductance of Metallic Alloys.* Metallic alloys may be divided into four classes which exhibit distinct properties.[13] These are: First, solid alloys in which pure crystals of the constituent elements are present in intimate contact; second, solid alloys in which mixed crystals of the constituent elements are present; third, solid alloys in which compounds of the constituent elements are present; and fourth, liquid alloys. Among the solid alloys, several of these types often appear in a single alloy. This is the case, for example, when mixed crystals are formed over limited concentration intervals.

a. *Heterogeneous Alloys.* Except in so far as the resistance of alloys is influenced by the distribution of the crystals and the presence of resistance at the interface between crystal elements, solid alloys of the first class do not differ in their properties from pure metals. The specific resistance of such alloys is a linear function of the composition and with change of temperature the properties vary as a linear function of the composition.

b. *Homogeneous Alloys.* Homogeneous mixed crystals of pure metallic elements, or of compounds, form an important class of substances which are remarkable for the uniformity of their behavior among themselves and the divergence of their behavior from that of their constituent elements. The addition of a second metallic component to another metal,

[11] Kraus, *Physical Review* 4, 159 (1914).
[12] Somerville, *Physical Review* 33, 77 (1911).
[13] A summary of the properties of metallic alloys is given by Guertler, *Jahrb. f. Rad.* 5, 17 (1908).

whether elementary or compound, causes a marked decrease in the conductance of the resulting homogeneous alloy. The decrease due to the addition of a given amount of the second constituent is the greater the lower its concentration. If the conductance is represented graphically as a function of the composition of the system, the resulting curve is throughout convex toward the axis of concentration. The minimum point in all cases lies in the neighborhood of a composition of 50–50. In

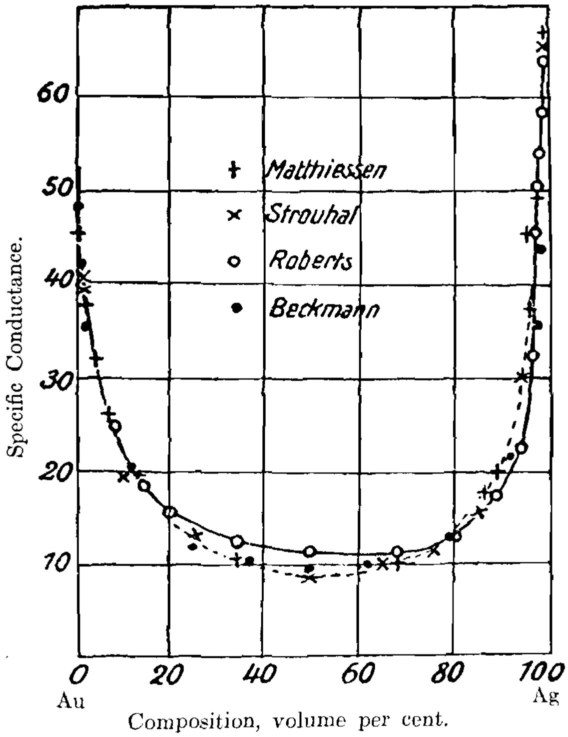

Fig. 68. Representing the Conductance of Homogeneous Alloys of Ag and Au as a Function of Composition.

Figure 68 is shown the conductance curve at ordinary temperatures for homogeneous mixtures of silver and gold. As may be seen, the conductance of either component is greatly reduced on the addition of the second constituent. The decrease in the conductance due to the addition of a second component depends upon the nature of the substance added and is, in general, the greater the less electropositive the added constituent. Thus, the decrease in the conductance of iron due to the addition of carbon or silicon is much greater than that due to the introduction of

tungsten or nickel. On the other hand, certain variations occur in the order of the effects. Thus, due to the addition of aluminium, the conductance of iron is lowered very nearly as much as due to that of silicon.

The resistance-temperature coefficient of solid alloys of the second class likewise varies continuously as a function of composition. The curve of temperature coefficients is similar to the conductance curve, being convex toward the axis of concentration and having a minimum point in the neighborhood of a composition of 50–50. In Figure 69 is shown the curve of temperature coefficients for alloys of silver and gold. It will

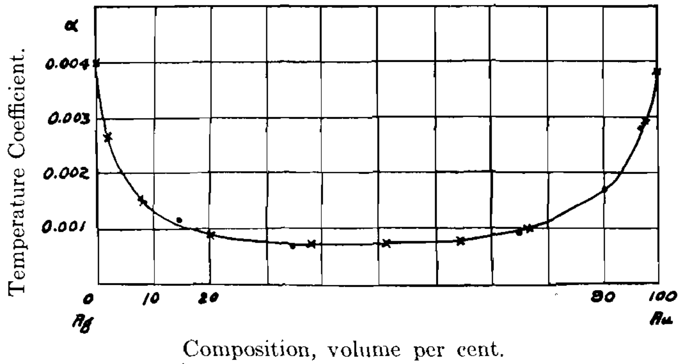

FIG. 69. Temperature Coefficient of Silver-Gold Alloys as a Function of Composition.

be observed that the temperature coefficient falls from a value of approximately 4×10^{-3} for the pure elements to 7.5×10^{-4} for an alloy containing 50 volume per cent, each, of the constituents. This behavior of homogeneous metallic alloys is general. In many cases, the effect is very pronounced and the temperature coefficient falls to very low values.

With decreasing temperature, particularly at low temperatures, the resistance of homogeneous metallic alloys decreases nearly as a linear function of the temperature. This form of the curve persists even to the lowest temperatures attainable. Apparently, then, the resistance of alloys of this type approaches a finite limiting value at the absolute zero. In the following table are given values of the resistance of manganin wire (84 Cu, 12 Mn, 4 Ni) down to liquid helium temperatures.

TABLE CLVIII.

RESISTANCE OF MANGANIN WIRE AT LOW TEMPERATURES.

Temp.	16.5	—193.1	—201.7	—253.3	—258.0	—269.0	—271.5
Resist.	124.20	119.35	117.90	113.42	112.91	111.92	111.71

:her alloys of this type exhibit a similar behavior at low temperatures.
At high temperatures, the resistance curves of many of the alloys of is type are very complex, often exhibiting both maxima and minima ıd the temperature coefficient at times becoming negative.[13a] The curve r manganin wire, for example, exhibits two maxima at approximately ° and 475° C. and two minima at 360° and 525° C. respectively. In a w instances, the temperature coefficient is very nearly zero over a large nge of temperature, as, for example, in the case of advance wire, for ıich the temperature coefficient varies very little up to a temperature of 0° C. Taken all together, the resistance curves of solid solutions of etals are very complex at higher temperatures.

c. *Solid Metallic Compounds.* The conductance of a solid compound two elements is always lower than that of one of the constituents and often lower than that of both. The specific resistance of a compound lative to that of the constituent elements depends upon the nature of e elements and upon tne nature of the compound formed. In general, e more stable the compound, the higher is its resistance relative to at of the constituent elements. Compounds between strongly electrositive and strongly electronegative metallic elements, as a rule, exhibit very high specific resistance. In the following table are given values the specific conductance of a number of compounds at room temratures.

TABLE CLIX.

SPECIFIC CONDUCTANCE OF A NUMBER OF METALLIC COMPOUNDS.

Metal	Mg_2Sn	Cu_2Mg	$CuMg_2$	$MgZn_2$	Mg_3Bi_2	Al_3Mn	Al_3Fe
$\times 10^{-4}$ ..	0.0912	19.4	8.38	6.3	0.76	0.20	0.71
Metal	Al_3Ni	AlMg	Al_2Mg_3	Al_2Ag_3	$AlAg_3$	Sb_2Te_2	TeSn
$\times 10^{-4}$ ..	3.47	2.63	4.53	3.85	2.75	0.48	0.97
Metal	Bi_2Te_3	$SbAg_3$	Cu_3As	MgAg	Mg_3Ag		
$\times 10^{-4}$ ..	0.045	0.93	1.70	20.52	6.16		

It will be observed, from the table, that the compound between magsium and tin has a very low specific conductance. Where two elents form a number of different compounds, that compound, in genal, has the lowest specific conductance which corresponds to the normal ectronegative valence of the less metallic element. Thus, the specific nductance of Cu_4Sn is much lower than that of Cu_3Sn or of CuSn. ıe low value of the specific conductance is well shown in the case of the oys of magnesium and tin which form the compound Mg_2Sn. The

[13a] Somerville, *Phys. Rev.* *31*, 261 (1910).

specific conductance of this compound at 25° is 0.0912, as compared with 8.65 for tin and 22.73 for magnesium.

While the conductance of inter-metallic compounds is thus, in general, very low, the temperature coefficient of these compounds is of the same order of magnitude as that of pure metals. While, therefore, the addition of a second metallic component increases the resistance of the metallic alloy, whether a compound or a solid solution is formed, so that it is at times difficult to distinguish between these two cases by this means, the temperature coefficient of the resulting alloy will, in general, differ widely in the two cases. The high value of the temperature coefficient of metallic compounds and the low value of this coefficient for homogeneous alloys afford a delicate method of detecting the presence of solid solutions in metallic alloys.

d. *Liquid Alloys.* The properties of liquid alloys differ greatly from those of homogeneous solid alloys. On the addition of a second component, the conductance of a liquid metal may either increase or decrease. The relative conductance of the two substances does not determine the magnitude and sign of the initial conductance change. If the specific conductance of two metals is nearly the same, the conductance curves often exhibit maxima or minima and sometimes both maxima and minima. In Figure 70 are shown the conductance curves for mixtures of mercury with bismuth, lead, tin and cadmium. Small additions of these elements to mercury cause a relatively large initial rise of the conductance curve. This rise is particularly noteworthy in the case of bismuth, which itself is a relatively poor conductor. The four curves are evidently similar. With bismuth and lead, whose specific conductances are relatively low, both a maximum and a minimum occur in the conductance curve. With tin the maximum and minimum have disappeared, but an inflection point is present in the conductance curve. The curve for alloys of cadmium and mercury exhibits a constant curvature. The four elements, the conductance of whose amalgams are shown in the figure, do not form compounds with mercury according to their melting point diagrams.

The behavior of amalgams, in which compounds are formed, differs markedly from that of amalgams in which compounds are absent. The addition of small amounts of lithium, calcium and strontium increases the conductance of mercury, while that of potassium, sodium, caesium and barium reduces its conductance.[14] With increasing temperature, the relative effect of such addition is increased. According to Hine,[15] the

[14] H. Fenninger, Dissertation, Freiberg, 1914; J. Koenigsberger, *loc. cit.*, p. 654.
[15] Hine, *J. Am. Chem. Soc.* *39*, 890 (1917).

specific conductance of sodium amalgams passes through a minimum at about 2.5 atom per cent of sodium. McCoy and West[15a] have determined the conductance of amalgams of substituted ammonium bases. The conductance of these amalgams decreases with increasing concentration, passing through a minimum. In general, liquid alloys whose components do not form compounds exhibit conductance curves without pronounced minima. On the other hand, alloys which form compounds often exhibit pronounced minima. This is, for example, the case with alloys of sodium and potassium. In the following table are given conductance values of mixtures of sodium and potassium, together with their temperature coefficients.[16]

TABLE CLX.

CONDUCTANCE OF LIQUID SODIUM-POTASSIUM ALLOYS AT 200°.

Atom Per Cent Potassium	Specific Conductance $\mu \times 10^{-4}$	$\alpha \times 10^3$
0	7.37	+3.85
4.2	5.55	3.222
8.0	4.42	2.43
26.5	2.690	1.725
44.5	2.150	1.555
63.0	2.095	1.585
82.0	2.250	1.860
93.0	3.230	2.91
100.0	4.59	4.98

It will be observed that the conductance curve exhibits a minimum in the neighborhood of 50 atomic per cent of sodium and potassium, which corresponds with the composition of the compound NaK. The existence of this compound has been established by means of the melting point diagram. It will be observed, also, that the temperature coefficient of the sodium-potassium alloys exhibits a minimum value at a composition corresponding with that of the compound. The conductance of alloys of copper and lead exhibits neither a maximum nor a minimum, but the temperature coefficient exhibits a minimum at a composition in the neighborhood of 40 per cent of lead. The conductance curves of liquid alloys of copper and antimony exhibit singularities corresponding with the composition of the compounds Cu_4Sb and Cu_3Sb. The temperature coefficients of both these compounds are negative, while those of the pure metals are positive. The conductance curve for liquid mixtures of copper

[15a] McCoy and West, *J. Phys. Chem.* 16, 261 (1912).
[16] Koenigsberger, *loc. cit.*

and tin likewise exhibits singularities, which indicate the formation of compounds. The temperature coefficients of these compounds are negative.

It may be concluded that liquid alloys, in which compounds are formed, exhibit properties which differ markedly from those of alloys in which compounds are not formed. When the compounds formed are very stable, the conductance of the resulting alloy is usually less than that of the pure components. The temperature coefficient of fused metallic compounds is, as a rule, either very small or negative.

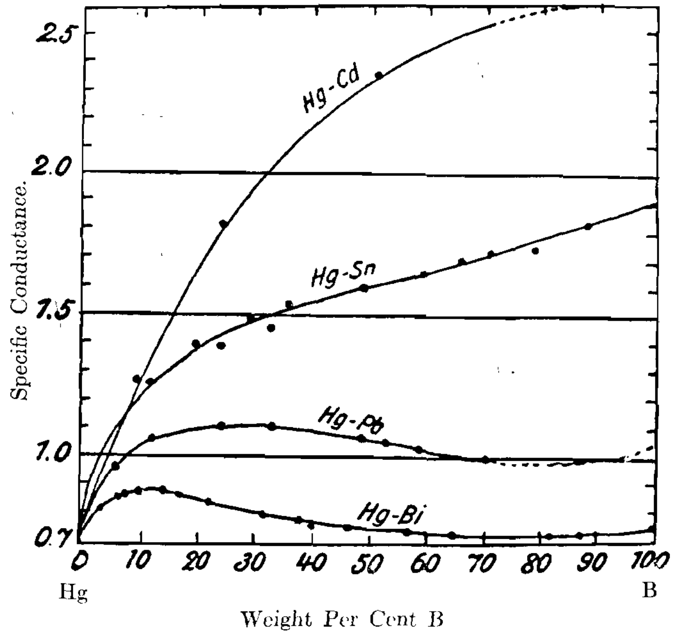

FIG. 70. Conductance of Liquid Amalgams as a Function of Composition.

6. *Variable Conductors.* Within this class are included those elementary substances which lie upon the border line between metallic and nonmetallic elements. There are also included a considerable number of metallic compounds in which one of the constituents is strongly electronegative. The elementary substances comprised within this class often appear both in a metallic and in a nonmetallic state. Carbon is a typical example of this type which, in the form of diamond, is a nonconductor, and, in the form of graphite, a relatively good conductor. Many of the metallic compounds, also, may appear both in a conducting and in a nonconducting state, as, for example, various sulphides and oxides

which are metallic in a crystalline state and which are nonmetallic when precipitated from solution.

The specific conductance of the metals of this class is often relatively low. In the following table are given values of the specific conductance of a few of these metals.

TABLE CLXI.

SPECIFIC CONDUCTANCE OF VARIOUS SUBSTANCES AT 0°.

Conductor	Specific Conductance
Graphite (Siberia)	8.71×10^2
Silicon (+ 3.3% impur.)	10.0
Titanium	2.8×10^3
Zirconium	5×10^3
CuS	8.5×10^3
PbO_2	4.3×10^3
CdO	8.3×10^2
PbS	4.2×10^2
Fe_3O_4	1.16×10^2
FeS_2 (Pyrite)	0.42×10^2
FeS_2 (Marcasite)	0.06

The resistance of metals of this class at lower temperatures decreases greatly with increasing temperature, approximately as an exponential function. At higher temperatures, the conductance reaches a minimum value, after which it increases approximately as a linear function of the temperature. A familiar example of this type of substance is carbon. It is uncertain, however, that the observed conductance curves of this type actually relate to pure substances. Kammerlingh Onnes and Hof [17] have shown, for example, that graphite may be purified to a point where its resistance decreases with temperature down to approximately — 173° with a coefficient of 0.0029. At lower temperatures the resistance decreases somewhat more rapidly. Similar results have been obtained in the case of bismuth. In the earlier experiments of Dewar and Fleming,[18] bismuth was found to exhibit a minimum resistance at temperatures varying from room temperatures to — 80° C., depending upon the purity of the sample. Later, however, this element was purified to a point where its resistance decreased throughout with decreasing temperature down to liquid hydrogen temperatures.[19] Since many of the substances of this class cannot be prepared readily in a pure state, it follows that the pecu-

[17] K. Onnes and Hof, *Koninklijke Akad, van Wetensch. Amsterdam 17,* 520 (1914).
[18] Dewar and Fleming, *Phil. Mag. 40,* 303 (1895).
[19] J. Clay, Dissertation, Leiden (1908) ; *Jahrb. f. Rad.* 8, 391 (1911).

liar form of the conductance curve may be due primarily to the presence of impurities.

Many of these substances exhibit transition points at which the resistance changes discontinuously. In some instances these processes are reversible and in others irreversible. Silicon exhibits transition points at approximately 220° and 440°. Titanium exhibits discontinuities in the neighborhood of 300° and 600°, the first of which is slowly reversible and the second irreversible.

Among variable conductors are included many compounds on the borderline between metallic and nonmetallic substances. These compounds often appear in several modifications whose properties may differ greatly. For example, silver sulphide, which has already been mentioned in a preceding chapter, conducts electrolytically in one form, while in another form it exhibits mixed electrolytic and metallic conduction. Many solid oxides and mixtures of oxides, which at ordinary temperatures are nonmetallic, appear to conduct the current metallically at high temperatures. The Nernst filament is a familiar example of this type of conductor. While it is possible that a portion of the current in some of these substances is carried electrolytically, the greater portion appears to be carried metallically.

As the compounds become more distinctively metallic, which is as a rule the case as the more electronegative element becomes more metallic and the more electropositive element becomes less metallic, the conductance approaches that of typical metallic compounds. In such cases, the temperature coefficient becomes less negative or even positive. In general, the higher the conductance of a compound, the greater is the value of its positive temperature coefficient.

Many of the conductors belonging to this class exhibit singular properties. In many cases, also, systems, which might not be expected to exhibit metallic properties, nevertheless belong to this class of conductors. Such is, for example, the case with cuprous iodide, CuI, which absorbs iodine reversibly. The resulting product conducts the current metallically and its conductance is the greater the greater the amount of iodine absorbed. The smaller the resistance of the iodide, the greater is the value of the positive temperature coefficient. As the specific resistance increases, the temperature coefficient becomes negative.

The examples of this class of substance are extremely numerous and a great deal of experimental material is available. It is not to be doubted that a study of such systems will throw a great deal of light on the nature of the conduction process and conceivably on the constitution of metallic

compounds. A more detailed discussion, however, is not possible in this monograph.[20]

7. *The Conductance of Metals as Affected by Other Factors.* a. *Anisotropic Metallic Conductors.* As might be expected, the conductance of many crystalline substances depends upon the orientation of the crystal. Thus, the conductance of a crystal of bismuth at right angles to its base at 15° is 1.78 times that parallel to its base.[21] It has been shown that the conductance of a bismuth crystal may be represented by means of an ellipsoid of rotation.[22]

b. *Influence of Mechanical and Thermal Treatment.* The conductance of metals is dependent upon their previous mechanical and thermal treatment. Wires which are hard drawn in general exhibit a lower conductance than do annealed wires. The thermal treatment of metals has an influence on their conductance, not only in that it tends to relieve mechanical stresses resulting from previous mechanical treatment, but also in that it tends to induce various transformations in the body of the metal, some of which are reversible and others of which are irreversible.

c. *The Influence of Pressure on Conductance.* The resistance of most metallic elements is decreased under the action of uniform pressure. The coefficient $\frac{1}{R}\frac{dR}{dp}$ for solid metallic elements varies between -15.1×10^{-7} for nickel and -152×10^{-7} for lead. For bismuth the value of the coefficient is positive and equal to $+196\times10^{-7}$. The resistance does not vary as a linear function of the pressure; the pressure coefficient decreasing with increasing pressure. The resistance of manganin wire varies very nearly as a linear function of the pressure. The only pure liquid metal for which data are available is mercury. At 25°, the value of its resistance-pressure coefficient is -334×10^{-7}. It would be interesting to know whether other liquid metals exhibit a similarly high value of this coefficient.

The influence of pressure on the resistance of variable conductors is often extremely marked.[23]

d. *Photo-electric Properties.* A few substances are sensitive to the action of light. Selenium is the most remarkable example of this type of substances. The influence of light and various other factors on the conductance of selenium has occupied the attention of a great many investigators. A detailed discussion cannot be given here.[24]

8. *Relation between Thermal and Electrical Conductance in Metals.*

[20] A very complete summary is given by Koenigsberger, *loc. cit.*, pp. 661-680.
[21] Lownds, *Ann. d. Phys.* *9*, 681 (1902).
[22] van Everdingen, *Versl. Akad. van Wetensch. Amsterdam* *3*, 316 and 407 (1900).
[23] For references, see Koenigsberger, *loc. cit.*, pp. 694-7.
[24] For references, see Koenigsberger, *loc. cit.*, pp. 681-694.

As was first pointed out by Wiedemann and Franz,[25] the thermal conductance of metals at ordinary temperatures is very nearly proportional to their electrical conductance. Subsequent investigations [26] have shown that the ratio of thermal to electrical conductance is not a constant, but increases with increasing temperature. Lorenz [27] showed that the ratio of thermal to electrical conductance $\frac{\lambda}{\mu}$ for pure metallic substances and some alloys increases approximately as a linear function of the absolute temperature, the coefficient being very nearly equal to the coefficient of expansion of gases. Since the resistance varies approximately as a linear function of the absolute temperature, it follows that the thermal conductance of metals is relatively independent of temperature. · At very low temperatures, however, the thermal conductance of metals increases markedly. Nevertheless, as K. Onnes and Holst [28] have shown, the thermal resistance of metals does not approach a value of zero in regions where metals are in the supraconducting state. For example, at its melting point, the thermal conductance of mercury is 0.075; between 4.5° K and 5.1° K it is 0.27; and between 3.7° K and 3.9° K it is 0.40. At very low temperatures, therefore, the thermal and electrical conductance do not follow a parallel course.

The thermal conductance of alloys varies with composition in a manner somewhat similar to that of the electrical conductance. The change in thermal conductance, due to a given change in composition, is considerably smaller than is the corresponding change in electrical conductance. The thermal conductance curves of alloys which form a complete series of mixed crystals exhibit a minimum similar to that of the electrical conductance curves. The relative decrease of the thermal conductance, however, is much smaller than that of the electrical conductance. Accordingly, the ratio of the thermal to the electrical conductance for homogeneous alloys is considerably greater than it is for pure metals. Somewhat similar relations are found in the case of metallic compounds. While compounds in general exhibit a lower thermal conductance than do the pure components, the ratio of thermal to electrical conductance is larger for the compounds than it is for pure metals.

The thermal conductance of variable conductors is often as great as that of typical metallic elements. Since the electrical conductance of these substances is relatively low, the ratio $\frac{\lambda}{\mu}$ for these substances is often

[25] Wiedemann and Franz, *Pogg. Ann. 89*, 497 (1853) ; *ibid., 95*, 338 (1895).
[26] The literature relating to this subject has been collected in various handbooks; see footnote, p. 385.
[27] L. Lorenz, *Pogg. Ann. 147*, 429 (1872) ; *Wied. Ann. 13*, 422 (1881).
[28] K. Onnes and Holst, *Proc. Amsterdam Acad. 17^1*, 760 (1914).

very great. Thus the value of $\frac{\lambda}{\mu}$ for graphite, silicon and hematite (Fe_2O_3) is 2.5×10^{12}, 6.8×10^{14} and 7.3×10^{14} respectively. For ordinary metals the value is in the neighborhood of 6.7×10^{10} at room temperatures.[29] In this connection it is interesting to note that the thermal conductance of some nonmetallic crystals is greater than that of many metallic substances. Thus, the thermal conductance of rock salt is 0.0137 and that of quartz ⊥ to its axis is 0.0263, while that of bismuth is 0.0194. While thermal and electrical conductance are intimately related, the fact that some nonmetals are likewise excellent thermal conductors should not be lost sight of.

9. *Thermoelectric Phenomena in Metals.* We have to consider three related thermoelectric phenomena, namely: 1, the electromotive force arising in a metallic system as a result of a temperature difference between the junctions of two metals; 2, the Peltier effect which is a heat transfer taking place when a current passes through a junction between two different metallic conductors; and, 3, the Thomson effect which is a heat transfer accompanying the passage of the current through a conductor in which a temperature gradient exists. From a practical point of view, the first of these effects is the most important and has been investigated most extensively.

The thermoelectric force of a thermocouple may be expressed very nearly as a function of the temperature by means of an equation of the form:

$$e_{AB} = \alpha t + \tfrac{1}{2}\beta t^2 + \cdots$$

Usually a quadratic equation suffices. For smaller temperature differences, the sign of the constant α corresponds with the direction of the thermoelectric force. The sign of this electromotive force depends upon the nature of the metals. Let us call the effect positive for the two metals AB, when the current flows from A to B at the cold junction. The metal A will then be said to be positive with respect to B. The values of the coefficients α and β for different metals with respect to lead, the cold junction being kept at a temperature of 0° C., are given in Table CLXII.

As may be seen from the table, metals which are closely related often have thermoelectric constants which are opposite in sign; thus, lithium and potassium stand in reverse order to lead, which, in the table, is taken as a standard. So, also, the closely related elements, antimony and bismuth, which exhibit a relatively high thermoelectric power, lie near

[29] See Koenigsberger, *loc. cit.*, p. 720.

TABLE CLXII.

VALUES OF THE THERMOELECTRIC COEFFICIENTS α AND β WITH RESPECT TO LEAD IN MICROVOLTS PER DEGREE.

Metal	Si	Te_{α}	Sb ‖	Fe	Li	Ag	Pb
α	+ 443	+ 163	+ 22.6	+ 13.4	+ 11.6	+ 2.3	0
$\beta \times 10^2$ ..	..	..	..	— 3.0	+ 3.9	+ 0.76	..
Metal	Mg	Sn	Na	K	Co	Ni	Bi ‖
α	— 0.12	— 0.17	— 4.4	— 11.6	— 20.4	— 23.3	— 127.4
$\beta \times 10^2$ ..	+ 0.20	+ 0.20	— 2.1	— 2.5	— 7.5	— 0.8	— 70.

the opposite ends of the table. Similar inversions are found in the case of other closely related elements, such as iron, cobalt and nickel.

In alloys, the thermoelectric force is, in general, a function of the composition. The thermoelectric force of heterogeneous alloys varies approximately as a linear function of the composition, while that of homogeneous alloys, in general, exhibits a marked minimum somewhat similar to that of the conductance curve. The thermoelectric power of a compound, in general, differs from that of its component elements. The formation of compounds by a given pair of elements is indicated by discontinuities in the curves connecting the thermoelectric force with the mean composition of the alloy. As a rule, the thermoelectric force is high for compounds which are relatively poor conductors. For a more detailed discussion of the thermoelectric properties of metals the reader is referred to the various handbooks in which these data have been collected.

10. *Galvanomagnetic and Thermomagnetic Properties.* When a current of electricity flows through a conductor, the distribution of the current in the conductor is altered under the action of an external magnetic field. The effects observed depend upon the relative direction of the current and of the field. The application of the magnetic field, therefore, gives rise to potential differences between points in the conductor which normally are at the same potential. With a field acting at right angles to the direction of the current flow, potential differences arise in the conductor transverse to the magnetic field, one at right angles to the direction of the current flow and the other parallel to this direction. With a longitudinal field, that is, a field acting parallel to the direction of the current flow, only a single effect is observable; namely, an electromotive force parallel to the direction of current flow. Similar effects are observed when a current of heat flows through a conductor in a mag-

netic field. Conversely, when a current flows through a conductor in a magnetic field, temperature differences, as well as potential differences, arise in the conductor. Altogether, there are twelve effects of this type: four thermomagnetic effects in transverse fields, two thermomagnetic effects in longitudinal fields, four galvanomagnetic effects in transverse fields, and two galvanomagnetic effects in longitudinal fields.

Of these various effects, the transverse galvanomagnetic effect in a transverse field has been studied most extensively. This is commonly known as the Hall effect. The relation between the electromotive force and the variables of the system are given by the equation:

$$e = \frac{RHi}{D},$$

where H is the field intensity, i is the total current flowing, and D is the thickness of the conducting sheet carrying the total current i. R, which is the constant of the Hall effect, is a property of the conductor in question. This constant varies greatly for different metals and may have either positive or negative values. As a rule, the effect is greatest in substances of relatively low conducting power. It is particularly marked in bismuth. Here, however, as might be expected, the value of the coefficient depends upon the orientation of the crystal. Since the flow of current in a conductor is influenced by an external magnetic field, it follows that the resistance of a conductor will be influenced by an external field.

At low temperatures, the influence of a magnetic field on the resistance becomes marked, particularly for bismuth. K. Onnes [30] has shown that at very low temperatures, where metals are normally in the supraconducting state, the curves connecting resistance and field strength are similar to those connecting resistance and temperature. The action of transverse and longitudinal fields differs little. For lead and tin the critical value of the field strength at which the resistance rises abruptly to measurable values lies between 500 and 700 G. It varies slightly with temperature.

The various galvanomagnetic and thermomagnetic effects would appear to be of great importance from a theoretical standpoint; for, if a current is carried by charged particles, the observed effects must be due to the reaction of the field on these particles. It might be expected that the reaction of the field on the moving particles in a metallic conductor would be similar to that observed in the case of the cathode rays. Actually, however, the observed effect in the case of most metallic conductors

[30] *Versl. Akad. van Wetensch. Amsterdam* 23, 493 (1914). See also J. Clay, *loc. cit.*

is in a direction opposite to that observed in the case of β particles, assuming that the conducting particles in metals are negatively charged. Since a great many facts indicate that the current in metallic conductors is not carried by positive particles, it appears that the various galvanomagnetic effects cannot be accounted for by a simple theory of this type. A number of theories, that of J. J. Thomson for example, have been suggested to account for the Hall effect and similar phenomena.[31] At the present time, however, a satisfactory theory of these effects does not exist. Indeed, the same may be said of the theory of the conduction process in metals under normal conditions. It may be expected, however, that ultimately the thermomagnetic and galvanomagnetic effects will play an important rôle in the development of the theory of metallic conduction.

A detailed study of the properties of conductors in a magnetic field would lead far beyond the scope of the present monograph. The observed facts will be found summarized in the references already given.

11. *Optical Properties of Metals.* According to the electromagnetic theory, the electrical and optical properties of metallic substances are intimately related. The reflecting power and absorbing power of metals, according to this theory, should be very great. From the known values of the conductance of metallic substances, the optical constants of these substances may be derived for long wave lengths when selective action does not occur.

The theory of the optical effects in metals, together with the most important facts, will be found summarized in treatises on electricity and magnetism and on physical optics.[32]

12. *Theories Relating to Metallic Conduction.* The theory of metallic conduction, like the theory of electrolytic conduction, is still in a very unsatisfactory state. Qualitatively, the theory that the current is carried by negative electrons is in good agreement with the facts, but a satisfactory quantitative theory has not, as yet, been established. The difficulties confronting a comprehensive theory of metallic conduction are, indeed, very great, as is apparent when it is considered how many detailed facts must be accounted for. A number of theories which have been proposed are able to account for a limited number of the properties of metals in a fairly satisfactory manner. So, for example, the theories of Drude and of Thomson render an account of the relation between the thermal and the electrical conductance of metals and, to some extent, also, of the thermo- and galvanomagnetic effects and thermoelectric effects in metals. On the whole, however, these theories are far from satisfactory. They

[31] J. J. Thomson, *Rapp. Congr. Phys.* 3, 143, Paris (1900).
[32] See, for example, Winkelmann, Handbuch d. Physik; Graetz, Handbuch d. Elektrizität u. d. Magnetismus, etc.

are not able to account for the properties of metallic substances at very low temperatures. Neither are they able to account successfully for the properties of alloys and of liquid metals.[33]

It is obvious that the electrical properties of metallic substances are extremely sensitive to all agencies. Temperature and density, as well as all external forces, have a marked influence upon the electrical properties of metals, and particularly on the conductance. So, also, the properties of metallic substances are very sensitive to change in the state of the system. The formation of compounds, of mixed crystals, or any polymorphic change is invariably accompanied by a great change in electrical properties. Ultimately, it would appear that a study of the electrical properties of metals, and particularly of metallic compounds, should yield some clue as to the constitution of these substances. At the present time, however, the constitution of metallic substances, and particularly of metallic compounds, remains an unsolved problem.

[33] Very complete references to the theories dealing with metallic conduction are given by Koenigsberger, *loc. cit.*, p. 385, above.

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